CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

Part I.

Organic Chemistry.

PART II.

General and Physical Chemistry.

Inorganic Chemistry.

Mineralogical Chemistry.

Physiological Chemistry.

Chemistry of Vegetable Physiology and Agriculture.

Analytical Chemistry.

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

C.

D.

E.

I.

J.

K.

R.

S.

ERRATA.

Vol. XCIX (Trans., 1911).

Page	Line.	
1662	10	*alter to* "In 1865, on Menschutkin's return to St. Peter he presented his."

Vol. XCIV (Abstr., 1908).

Part II.

Page	Col.	Line.	
1131	ii	5	*for* "A., ii, 590" *read* "A, i, 590."

—*The Active Constituents of the Indian olanaceous Plants* Datura Stramonium, D. stuosa, *and* D. Metel.

By Albert Edward Andrews.

JGH the solanaceous plants *Datura Stramonium*, *D. fastuosa*, *Metel* grown in Europe have been investigated by several s, yet with the single exception of an article in the tin of the Imperial Institute" (1905, **2**, 224) giving the of the examination of a specimen of *Datura Stramonium* no chemical investigation of these plants as grown in India s to have been published, notwithstanding that their nal and poisonous properties have long been recognised in ountry. For this reason, and with a view to their possible rcial utilisation, samples of these plants have from time to een investigated in the Scientific and Technical Department Imperial Institute, and it is thought that it would be of t to record the results obtained, especially as differences of e and soil are known to produce considerable alteration in the uents of plants. In carrying out this investigation, the chief as been to determine the amount and nature of the alkaloidal uents, and compare them with those from the same species elsewhere.

Indian species of *Datura* grow wild, and have long been to the people of India for their intoxicating and narcotic ties. *D. Stramonium* is met with in the temperate Himalaya Baluchistan and Kashmer to Sikkim. *D. fastuosa* is a small found all over the tropical parts of India, and is said to be ost common and abundant species. *D. Metel* grows chiefly e North-West Himalaya and the mountains of the Deccan.

material used in the present investigation was kindly sent e Officiating Reporter on Economic Products to the Government of India at the instance of Professor Wyndham R. Dunstan, whose direction this work has been carried out.

Experimental.

Extraction and Estimation of the "Total Alkaloid."

e following was the general method employed in the examination of the various samples:

e finely ground material is exhausted by percolation with cold ol, and the solvent distilled off under diminished pressure until

practically the whole has been removed. The semi-solid ext well agitated with small quantities of warm water, and then with very dilute sulphuric acid to ensure the complete sepa of the alkaloid. The filtered aqueous acid liquid is shaker ether, then made weakly alkaline with dilute ammonia, and s several times with chloroform to extract the alkaloid. Each p of chloroform used to extract the alkaloid is in turn transfer a second separator, washed with a little water, then driec anhydrous sodium sulphate, and the total chloroform e distilled under diminished pressure at a temperature not exc 40°. The total crude alkaloid thus obtained is then purifiec at the same time separated into two fractions. The resic alkaloid is dissolved in a small excess of very dilute sulphuri and the solution, filtered if necessary, is shaken with eth remove traces of colouring matter and other impurities solub ether; the aqueous liquid is then made slightly alkaline with c ammonia, and extracted with three or four portions of ether then with chloroform. Both the ether and chloroform solutic the alkaloid are washed and freed from water as before noted the two fractions of alkaloid obtained by the distillation o solvents are dried in a vacuous desiccator and weighed. combined weights of the two extracts give the "total alka contained in the sample.

The separation of the total alkaloid into two fractions is don a preliminary step in the identification of the constituent alkal for should more than one alkaloid be present a partial separati obtained, and the identification of the alkaloids facilitated.

The Identity of the Alkaloids.

In cases where hyoscyamine is the only alkaloid, or else la predominates, the crystalline nature of the fraction extracted chloroform indicates its presence; otherwise, the total alkaloi weighed is amorphous. The aurichlorides are next prepared each of the two fractions, and this salt is then fractionally cry lised until fractions of definite melting point are obtained. alkaloids are then recovered from these fractions, and are fur examined, following the clue to their identity given by the me points of the gold salts.

In the case of scopolamine the identity was established by melting points and general properties of the aurichloride, hy bromide, and picrate, as compared with the same salts prep and examined under identical conditions from a sample of Me scopolamine hydrobromide represented as agreeing with E. Schm alkaloid, and also with the tests of the German Pharmacop

was complete agreement between the scopolamine isolated the different plants and this sample of alkaloid.

 hyoscyamine isolated from the different plants in the course is investigation was obtained in white, lustrous, hair-like ls, melting at 106°, and having $[\alpha]_D -20{\cdot}75°$ at 21°. The ing salts were prepared:

The aurichloride	melting at	159·5°.
The hydrobromide	,, ,,	149—150°.
The sulphate	,, ,,	209—210°.
The picrate	,, ,,	162—163°.

will be seen from the tabulated results, there was no indica- of atropine in any of the *Datura Stramonium* or *D. fastuosa* les. In the case of *D. Metel*, however, there was evidence of

lts of examination of *Datura Stramonium* samples from the Punjab.

of plant.	Percentage of total alkaloid. In material as received.	Percentage of total alkaloid. Calculated on water-free material.	Alkaloids present.	Remarks.
s of small it	0·23	0·25	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 3 or 4 to 1 respectively
ns of large nt	0·23	0·26	Hyoscyamine and scopolamine	There appeared to be rather less scopolamine present than in the previous samples
ves of small nt	0·42	0·45	Hyoscyamine only	There was no indication of the presence of any other alkaloid
ves of large nt	0·38	0·41	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 4 to 1 respectively
its of small ant	0·42	0·46	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 4 to 1 respectively
its of large ant	0·43	0·46	Hyoscyamine only	There was no indication of the presence of any other alkaloid
ots* of both rge and small lants	0·19	0·21	Hyoscyamine and scopolamine and another alkaloid not identified	The hyoscyamine and scopolamine were present in about equal quantities
ry small complete plant	0·20	0·22	Scopolamine only	There was no indication of the presence of any alkaloid other than scopolamine

* The large quantity of potassium chloride and nitrate present in this sample was rticularly noticeable. The alcoholic percolate was found to contain an amount of se salts which, calculated as K_2O, equalled 1·42 per cent. of the roots.

Results of examination of *Datura Stramonium* samples fr Madras.

Part of Plant.	Percentage of total alkaloid. In material as received.	Calculated on water-free material.	Alkaloids present.	Remarks.
Leaves	0·38	0·42	Hyoscyamine and scopolamine	These alkaloids present in the [tion of about : respectively
Seeds	0·173	0·186	Hyoscyamine and scopolamine	These alkaloid present in the [tion of about respectively. was in addit small quantity pure alkaloid, ably hyoscyami

the presence of a small proportion of atropine, but the amount insufficient fully to establish its identity. In these cases the a chloride was obtained in non-lustrous crystals, melting at 135—1 and the alkaloid recovered from these was optically inactive.

The tabulated statements give the results obtained with different parts of the Indian solanaceous plants, *Datura Stramon* *D. fastuosa*, and *D. Metel*, and show (1) the amount of total alka contained in the particular part of the plant, (2) the constitu alkaloids which have been identified, and (3) the approxim proportions of the different alkaloids in those cases where m than a single alkaloid is present.

The following points may be noted from the tabulated re for the *Datura Stramonium* samples:

In the samples from the Punjab the percentage of total alka in similar parts of the large and small plants was practically same, whether in the fruits, stems, or leaves.

The alkaloids in all of the samples were either hyoscyamine scopolamine, or both in varying proportions. Only in the c of the roots was there evidence of a third alkaloid. There was indication of atropine in any of the samples.

Hyoscyamine was the only alkaloid found in the leaves of t small plant and in the fruits of the large plant. In each case was present to the extent of nearly 0·5 per cent., and could read be isolated in a crystalline condition.

Scopolamine was the only alkaloid in the very small plant. W this one exception, hyoscyamine was the predominant alkalo The proportion of hyoscyamine and scopolamine in the stems the large and small plants shows very little variation, but in t

the fruits and the leaves it is noticeable that scopolamine it in the leaves of the small plant and in the fruits of the lant. The following table showing the distribution of the ls in the different parts of the small and large plants es these points more clearly. It should be mentioned that plants were collected at one time in the same district of the b.

	Stems.	Leaves.	Fruits.	Whole plant.	
mall	—	—	—	Scopolamine	
	3 or 4 parts of hyoscyamine to 1 part of scopolamine	Hyoscyamine only	4 parts of hyoscyamine to 1 part of scopolamine	—	Hyoscyamine and scopolamine in about equal proportions, and a small proportion of a third alkaloid not identified
	Hyoscyamine and scopolamine. Rather less of the latter alkaloid than in stems of small plant	4 parts of hyoscyamine to 1 part of scopolamine	Hyoscyamine only	—	

the following table the percentages of total alkaloid found Indian specimens of *Datura Stramonium* are compared with corded figures for similar parts of the plant grown elsewhere:

of plant.	Indian specimens.	Specimens from other countries.		
Seeds	0·186	0·21 to 0·43 (European)		
	0·46*	0·35 (Egyptian)		
Leaves	0·41 to 0·45	Up to 0·4 (European)		
Stems	0·25 to 0·26	Main stems	0·09	(European)
		Upper branches	0·36	
		Average	0·22	
Roots	0·214	Main roots	0·10	(European)
		Rootlets	0·25	
		Average	0·17	

his was the percentage in two samples of the fruits, that is, seeds and s together; the alkaloid is chiefly present in the seeds, consequently the or the fruits is lower than it would be for the seeds alone.

hese figures clearly indicate that Indian *Datura Stramonium* favourable comparison with the European and Egyptian s as regards the amount of total alkaloid that it contains. he plants from the latter sources, hyoscyamine is generally d to be the only or the main alkaloid present, being in some associated with a small proportion of atropine. The presence opolamine in some of the Indian samples appears, therefore, a point of difference.

Results of examination of *Datura fastuosa* var. black, from Assam.

Part of plant.	Percentage of total alkaloid in material as received.	Alkaloids present.	Remarks.
Twigs and leaves	0·119	Scopolamine and hyoscyamine	These alkaloids were present in the proportion of about 4 to 1 respectively. There was in addition a small proportion of amorphous alkaloid
Roots	0·101	Scopolamine only	There was no indication of either hyoscyamine or atropine. A small proportion of amorphous alkaloid was present
Fruits	0·202	Scopolamine only	There was no indication of either hyoscyamine or atropine. A small proportion of amorphous alkaloid was present

It is noticeable in the above results for *D. fastuosa* that scopolamine is the only alkaloid in the roots and fruits, and is the predominant alkaloid in the twigs and leaves of the plant. The seeds of this species grown in Europe contain about the same amount of alkaloid as that found for the Indian plant, and contain scopolamine as the main alkaloid associated with a small proportion of hyoscyamine and a little atropine.

Results of examination of *Datura Metel* samples from the Punjab.

Part of plant.	Percentage of total alkaloid. In material as received.	Percentage of total alkaloid. Calculated on water-free material.	Alkaloids.	Remarks.
Leaves from Lyallpur	0·22	0·25	Scopolamine	A small proportion of another alkaloid, apparently atropine, was present
Seeds from Lyallpur	0·21	0·23	Scopolamine	Ditto
Seeds from Patiala	0·23	0·25	Hyoscyamine and scopolamine	These alkaloids were present in the proportion of about 2 to 1 respectively. A small proportion of another alkaloid was present, which appeared to be atropine
Capsules from Patiala	0·10	0·12	Scopolamine only	No indication of the presence of any other alkaloid

E. Schmidt (*Arch. Pharm.*, 1905, **243**, 309; 1910, **248**, 641) examined *D. Metel* cultivated in France, and found that scopolamine is present in all parts of the plant and is unaccompanied by any notable quantity of other mydriatic bases. The dried leaves

contain 0·55 per cent., and the seeds 0·5 per cent., of scopolamine. Kircher (*Arch. Pharm.*, 1905, **243**, 309) confirmed Schmidt's figures, and drew the conclusion that scopolamine formed the bulk of the alkaloid, being accompanied by only small proportions of hyoscyamine and atropine.

On comparing these results with those in the table, it appears that in the Indian plant the percentage of total alkaloid in the seeds and in the leaves is only about one-half what it is in the European plant. The *D. Metel* seeds from Patiala appear to be exceptional in containing hyoscyamine as the predominant alkaloid, but the other three samples resemble the European plant in so far that scopolamine is almost unaccompanied by other mydriatic alkaloids.

SCIENTIFIC and TECHNICAL DEPARTMENT,
IMPERIAL INSTITUTE, S.W.

CCXI.—*A New Stereoisomeride of Cyanodihydrocarvone.*

By ARTHUR LAPWORTH and VICTOR STEELE.

IT has been shown that *d*-carvone unites with hydrogen cyanide in the presence of potassium cyanide at the ordinary temperature, yielding, in the first instance, a cyanodihydrocarvone:

$$\underset{(2)}{CH_3\cdot CH}<\begin{matrix}CO\text{——}CH_2\\ \underset{(3)}{CH(CN)}\cdot CH_2\end{matrix}>\underset{(1)}{CH}\cdot C<\begin{matrix}CH_3\\ CH_2\end{matrix}.$$

This substance contains three asymmetric carbon atoms, labelled 1, 2, and 3, whilst the original carvone contains the first only (Trans., 1906, **89**, 945 *et seq.*, and 1819 *et seq.*). *d*-Carvone may theoretically give rise to four stereoisomeric cyanodihydrocarvones, and evidence of the existence of at least two was obtained on a former occasion by showing that the one which had then been isolated in a pure form exhibited mutarotation in the presence of a trace of sodium ethoxide. It has since been observed that if the addition of the hydrogen cyanide takes place in hot solutions, a crystalline cyanodihydrocarvone is formed in considerable quantity, which has a rotatory power in the opposite sense to that of the isomeride previously described, and cannot be converted into the latter by traces of alkali. It is probable that it represents the third possible isomeride, and it appears to be partly converted into the fourth isomeride by small quantities of alkali in alcoholic

solution, as it then exhibits a small but definite mutarotation; the final value of the rotatory power attained is, however, about $[\alpha]_D -39.00°$ instead of $[\alpha]_D +15.4°$, the value shown by the cyano-compound first discovered.

It would thus appear that the four isomerides may be divided into two pairs, the two members of each pair being dynamic isomerides at the ordinary temperature. At higher temperatures, in the presence of alkalis, all four are probably dynamic isomerides, as in this case hydrogen cyanide may be alternately eliminated and reabsorbed with considerable rapidity. It is known that the sign of an asymmetric carbon atom in the complex $\genfrac{}{}{0pt}{}{a}{b}\!\!>\!CH{\cdot}CO{\cdot}C\vdots$ may undergo inversion, causing the effect of mutarotation in the presence of traces of alkalis. As the hydrogen atom in the group $>CH{\cdot}CN$ appears usually to be less labile than that in the group $>CH{\cdot}CO{\cdot}C\vdots$, it appears highly probable that the mutarotations observed with the two crystalline cyanodihydrocarvones at the ordinary temperature may be attributed to the presence of the latter complex. If this is so, then the new cyano-compound and its dynamic isomeride differ from those obtained by the synthetic process at the ordinary temperature, by a change in the sign of the asymmetric carbon atom to which the cyano-group is attached. It was proved that the asymmetric carbon atom of the carvone complex itself had been unaffected, as both the crystalline cyano-compounds yielded pure *d*-carvone when boiled with solutions of alkali containing suspended ferrous hydroxide.

The new nitrile yields a new *amide* when hydrolysed by cold hydrogen chloride, but the carboxylic acids which are formed on further hydrolysis are identical with those previously obtained.

EXPERIMENTAL.

neo-*Cyanodihydrocarvone*, $C_{11}H_{15}ON$.

This substance was accidentally obtained, in the first instance, as the result of using a hot, instead of a cold, solution of potassium cyanide during the preparation of α-cyanodihydrocarvone by the process otherwise as previously described (Trans., 1906, **89**, 950), the yield being very small. It was found later that the following process gave yields of about 85 per cent. of the theoretical.

Thirty grams of potassium cyanide (100 per cent.), 80 c.c. of water, and 80 c.c. of spirit are together heated to boiling on the water-bath, and a boiling mixture of 60 grams of carvone and 30 c.c. of ethyl acetate is then added, heating being continued until complete solution takes place, an operation which usually occupies

about twelve to fifteen minutes. The whole is cooled and diluted with water, when the greater part of the nitrile separates in a solid form, and is removed by filtration, the filtrate being extracted with ether. The ethereal extract is washed with water, the solvent removed, and the residue added to the precipitated nitrile. The compound is purified by repeated crystallisation from alcohol:

0·2018 gave 0·5500 CO_2 and 0·1549 H_2O. C=74·3; H=8·3.
$C_{11}H_{15}ON$ requires C=74·6; H=8·5 per cent.

Experiments were made with the object of ascertaining whether the β-cyanodihydrocarvone could be obtained from the α-nitrile by the action of small quantities of alkalis or sodium ethoxide, but although change certainly occurs, the oils which are formed do not readily yield anything of a definite character. β-Cyanodihydrocarvone resembles its isomeride in regard to its behaviour towards the usual solvents, and crystallises from alcohol or benzene in needles, melting at 84°.

0·3618, made up to 25 c.c. with absolute alcohol, gave, in a 2-dcm. tube, $\alpha - 1·22°$, whence $[\alpha]_D - 42·1°$. After the addition of a trace of sodium ethoxide, the observed rotation was $-1·13°$, whence $[\alpha]_D^{11} - 39·00°$. That this slight fall was in the main due, as is the case of its isomeride, to isodynamic change seems probable, as the solution on spontaneous evaporation yielded a viscid liquid which crystallised only after some time; the solid then obtained was, however, identical with the original substance (compare Trans., 1906, **89**, 951).

The nitrile distils under the ordinary pressure without undergoing any appreciable isomeric change, but with slight charring. It behaves towards potassium permanganate and bromine as an unsaturated compound, exhibits distinct basic properties, dissolving appreciably in concentrated hydrochloric acid, and is not precipitated from the solution on addition of water. Although it is not quickly decomposed by a hot 5 per cent. solution of potassium hydroxide in alcohol, it rapidly loses hydrogen cyanide when boiled with concentrated alcoholic potassium hydroxide, carvone being liberated, and the change is more rapid and complete if ferrous hydroxide is also present to unite with the potassium cyanide as it is formed. In one experiment this nitrile was heated with a concentrated methyl-alcoholic solution of potassium hydroxide containing suspended ferrous hydroxide, for about fifteen minutes, the liquid being then diluted with water and distilled in a current of steam. The distillate was extracted with ether, the ethereal solution washed with a little water, dried, and freed from solvent. On distillation of the residue, the fraction boiling at 225° was collected;

this had the odour of ordinary carvone, and had the same rotatory power.

0·335, made up to 25 c.c. with absolute alcohol, gave, in a 2-dcm. tube, $\alpha + 1·68°$, whence $[\alpha]_D^{13} + 62·7°$, whilst carvone has $[\alpha]_D + 62°$ to $62·5°$ in this solvent.

The action of amyl nitrite and sodium ethoxide on the new nitrile was investigated.

Twelve grams of the pure nitrile were added to an ice-cold solution of 1·6 grams of sodium dissolved in 40 c.c. of absolute alcohol; 10 grams of amyl nitrite were then added slowly, the temperature being kept at 0°. After twelve hours, water (500 c.c.) was added, and the solution filtered from a little tarry matter. The filtrate was saturated with carbon dioxide, when a white, voluminous solid separated. This was collected, and after crystallisation from alcohol weighed 11 grams. It crystallised in slender needles, melting at 138—139°, and was identical with the active lactam obtained by Lapworth and Wechsler (Trans., 1907, **91**, 981) by a similar treatment of ordinary cyanodihydrocarvone; thus its melting point was not affected by admixture with that compound, and its rotatory power had the same value.

0·2055, made up to 25 c.c. with absolute alcohol, gave, in a 2-dcm. tube, $\alpha + 1·99°$, whence $[\alpha]_D^{14} + 121·04°$.

The compound described by Lapworth and Wechsler had $[\alpha]_D + 121°$ in alcohol.

The *phenylhydrazone*, $CN·C_{10}H_{15}:N·NHPh$, was prepared by warming together equimolecular proportions of the nitrile and phenylhydrazine for half an hour. It was purified by crystallisation from alcohol:

0·1836 gave 0·5075 CO_2 and 0·1305 H_2O. C = 75·4; H = 7·9.

$C_{17}H_{21}N_3$ requires C = 75·4; H = 7·9 per cent.

It closely resembles the isomeric hydrazone previously described (*loc. cit.*, p. 952), but separates from alcohol in slender needles, and is somewhat unstable, changing spontaneously into a dark red syrup. It melts and decomposes between 113° and 116°, according to the rate of heating.

The *oxime*, $CN·C_{10}H_{15}:NOH$, crystallises from alcohol in flat needles, which melt at 182° with slight darkening. In other respects, it has much the same properties as the oxime of the α-cyanodihydrocarvone:

0·1993 gave 0·5007 CO_2 and 0·1512 H_2O. C = 68·5; H = 8·4.

$C_{11}H_{16}ON_2$ requires C = 68·7; H = 8·3 per cent.

Formation of Carboxylic Acids from β-Cyanodihydrocarvone.

Five grams of nitrile were left in contact with 40 grams of saturated aqueous hydrogen chloride for five days, the hydrolysis being completed by heating for two hours on the water-bath. The acid products of hydrolysis were finally obtained as a crystalline mass, which was rapidly washed with carbon disulphide. A colourless mass was left, which was crystallised from ethyl acetate:

0·1620 gave 0·3997 CO_2 and 0·1190 H_2O. C = 67·3; H = 8·2.

$C_{10}H_{15}O{\cdot}CO_2H$ requires C = 67·4; H = 8·2 per cent.

0·1463 required 7·5 c.c. $N/10$-NaOH for neutralisation, using phenolphthalein as indicator, hence equivalent = 195. The number calculated for a monobasic acid, $C_{11}H_{16}O_3$, is 196.

The product, as in the case of the hydrolysis of α-cyanodihydrocarvone, was found to be a mixture, the melting point being indefinite between 85° and 110°. As the whole did not melt below 100°, the mixture was placed on porous porcelain, and allowed to remain in the steam-oven for four hours. A small quantity of material was left, which appeared to be homogeneous, and after one or two crystallisations melted sharply at 135°. The quantity obtained in a pure state, however, was too small for further investigation.

On another occasion the crude product of hydrolysis was extracted repeatedly with boiling water, a treatment which left a dark-coloured, insoluble gum behind. On cooling the extract, the acids crystallised as a mixture of pure white needles and flat plates. By crystallisation from carbon tetrachloride, two fractions were obtained, the first being only sparingly soluble, and the other fairly readily so in that solvent. The first fraction was recrystallised, and separated in plates, melting sharply at 142—143°; it was proved to be identical with the β-acid obtained from ordinary cyanodihydrocarvone by the "mixed melting-point" method. The other fraction was crystallised twice from ethyl formate, and then melted sharply at 97°; it was proved to be identical with the α-acid obtained from ordinary cyanodihydrocarvone.

β-Cyanodihydrocarvonecarboxylamide, $NH_2{\cdot}CO{\cdot}C_{10}H_{15}O$.—The nitrile (5 grams) was allowed to remain with saturated hydrobromic acid (10 c.c.) until it had dissolved, and a drop of the resulting liquid gave no precipitate on addition to water, when, on diluting with water and neutralising with sodium carbonate, the amide slowly separated in crystalline form. It was purified by crystallisation from alcohol:

0·2187 gave 0·5452 CO_2 and 0·1699 H_2O. C = 67·9; H = 8·6.

$C_{11}H_{17}O_2N$ requires C = 67·7; H = 8·7 per cent.

The amide, which closely resembles its isomeride in solubility in organic media, separates from ethyl acetate in flat needles, which, when heated, darken slightly at 200°, and melt at 218°. When it was mixed with the amide obtained from the α-nitrile, melting occurred at 180°, so that the compounds are not identical.

When the new amide is almost fully hydrolysed by means of hot alcoholic potassium hydroxide, the acidic product is a mixture of α- and β-dihydrocarvonecarboxylic acids. If, however, the heating occupies only a few minutes, and the resulting liquid is poured into water and acidified, a crystalline precipitate of an acid is obtained, which, after one crystallisation from water, melts at 141—142°, being practically pure α-dihydrocarvonecarboxylic acid, as was shown by the "mixed melting-point" method. It has previously been shown (Trans., 1906, **89**, 958) that the amide obtained from ordinary cyanodihydrocarvone, if hydrolysed by boiling with alcoholic potassium hydroxide, is converted into a dihydrocarvonecarboxylic acid. These experiments have since been repeated, the whole being heated for a short time only; the product, after one crystallisation from water, melted sharply at 97°, and was identical with the β-carboxylic acid, whilst the nearly pure α-acid was obtained on a former occasion by one of us.

The observations as to the conditions which lead to the production of either or both carboxylic acids from the isomeric amides are thus somewhat contradictory, so that the relationship between the compounds remains an open question.

SCHUNCK LABORATORY,
UNIVERSITY OF MANCHESTER.

CHEMICAL LABORATORY,
GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

CCXII.—*Some Properties of Phenyl* iso*Propyl Ketone.*

By ARTHUR LAPWORTH and VICTOR STEELE.

IT is well known that ketones which contain the group $\cdot CO\cdot CH_2\cdot$ condense readily with certain carboxylic esters in presence of sodium or sodium ethoxide, yielding β-diketones and alcohol, whilst ketones which contain only the complex $\cdot CO\cdot \dot{C}H$ do not take part in such a condensation. The theory of the mechanism of the reaction has been discussed on numerous occasions, and reference may be made to a paper by Clarke, Lapworth, and Wechsler (Trans., 1908, **93**, 30) for an historical summary.

With the view of obtaining some further evidence on the subject, the behaviour of phenyl *iso*propyl ketone towards such reagents has been investigated, as it was thought possible that this ketone might react with certain carboxylic acids in accordance with the following scheme (compare 1 (*b*), *loc. cit.*, p. 34):

$$R\cdot CO\cdot OEt + CHMe_2\cdot COPh \longleftrightarrow R\cdot CO\cdot CMe_2\cdot COPh + HOEt$$
$$\longleftrightarrow R\cdot CO\cdot CHMe_2 + OEt\cdot COPh$$

yielding ethyl benzoate and a new ketone.

The ketone used in the first experiment was prepared from *iso*butyryl chloride and benzene by the Friedel-Crafts' reaction, and the acid chloride itself from a sample of calcium *iso*butyrate. When this ketone, after careful fractionation, was brought into contact with sodium and ethyl acetate, formate, benzoate, or oxalate, in ethereal solution, highly coloured liquids were produced, which, when shaken with water, yielded yellow aqueous extracts, from which acids precipitated small quantities of acidic oils. The latter gave violet or deep-brown colorations with ferric chloride, and, in general, deported themselves as β-diketones or β-ketonic esters.

Later the ketone was allowed to react with ethyl phthalate and sodium, as the ketonic compound, which would arise as the result of the above series of reactions, would then have had the structure (I), from which an acid could be obtained and easily identified,

$$C_6H_4<\begin{matrix}CO\cdot CHMe_2\\ CO_2Et\end{matrix} \qquad\qquad C_6H_4<\begin{matrix}C(:CMe_2)\\ C(:NOH)\end{matrix}>O$$

(I.) (II.)

even if formed in comparatively small quantities, by means of its characteristic oxime-anhydride (II).

A red solution was formed in the cold, and to this alcoholic potassium hydroxide was added, and the whole heated for several hours on the water-bath, the ether being allowed to escape; hydroxylamine hydrochloride was then added, when, on cooling, a small quantity of a compound separated, which was at first thought to be the expected oxime-anhydride. It was collected, crystallised from alcohol, and analysed:

0·1996 gave 0·5009 CO_2 and 0·0921 H_2O. C = 68·3; H = 5·2.

$C_{10}H_9O_2N$ requires C = 68·0; H = 5·1 per cent.

It thus had the composition of *ethylidenephthalideoxime*,

$$C_6H_4<\begin{matrix}C(:CHMe)\\ C(:NOH)\end{matrix}>O,$$

and melted at 111°; its identity with that compound was established by preparing a sample of the latter from synthetical ethylidenephthalide and hydroxylamine; the compounds were identical in all respects, and mixtures melted at the same temperature as either separately.

The formation of this substance in the above reaction suggested that the original ketone contained phenyl ethyl ketone, owing to the unsuspected presence of propionate in the sample of calcium *iso*butyrate. Repeated fractionation of the ketone did not serve appreciably to diminish its reactivity towards esters and sodium, and the whole was therefore converted into oxime, the latter carefully purified, and reconverted into ketone by the processes described below. When purified in this way, the ketone displayed complete indifference towards carboxylic esters (including ethyl phthalate) in presence of sodium even at the temperature of the water-bath; that is to say, no trace of ketonic compound other than the original one could be detected.

It must be concluded, therefore, either that phenyl *iso*propyl ketone does not react at all with carboxylic esters in the presence of sodium or sodium ethoxide, or that the product decomposes exclusively into its original generators. It would be interesting to ascertain whether di*iso*propyl ketone would react with ethyl phthalate and sodium yielding *iso*propylidenephthalide and ethyl *iso*butyrate, but this the authors have not had the opportunity to test.

Preparation of Ketoximes and their Use in the Purification of Ketones.

Phenyl iso*Propyl Ketoxime.*

Some five years ago the authors devised the following process for preparing oximes, and using these for the purification of ketones; as the methods have proved to be of very general applicability, the more important details may be given here.

In preparing oximes the main practical advance consisted in avoiding the use of water other than that possibly contained in the solvent alcohol; the quantity of solvent then necessary is, as a rule, greatly diminished, whilst the use of sodium acetate precludes the possibility of any appreciable hydrolysis or transformation of the oxime formed.

The ketone is dissolved in at least three times its weight of spirit of 94—100 per cent. strength, the quantity and percentage of solvent depending mainly on the solubility of the ketone in the boiling solvent. To the hot solution is added 1 to $1\frac{1}{2}$ molecular proportions of solid hydroxylamine hydrochloride, and then at once excess of anhydrous sodium acetate; sodium chloride separates, but the whole is heated (at a temperature somewhat below that likely to cause bumping) until a drop of the solution, added to about $\frac{1}{2}$ c.c. of 10 per cent. sodium hydroxide, gives a clear solution

with no odour of ketone. The whole is cooled, evaporated, if necessary, in cases where the ketone is sparingly soluble, and the bulk of solvent therefore considerable, mixed with water, and the oxime removed by filtration or by extraction with light petroleum or ether. Nearly quantitative yields have been obtained with most simple ketones experimented with, and such compounds as camphor-oxime are prepared much more easily and economically by this process than by those usually recommended. Crossley and Renouf found that a modification of this method gave good results with dimethyldihydroresorcin (compare Trans., 1909, **95**, 930, *footnote*), and it might with great advantage replace the older methods in nearly all cases.

The regeneration of the ketone from the pure oxime is accomplished most satisfactorily as follows. The oxime is heated for several hours on the water-bath with 3 to 4 parts by weight of 15 per cent. hydrochloric acid, and $\frac{1}{2}$ to $\frac{3}{4}$ part by weight of commercial formaldehyde (40 per cent.); the whole is cooled, poured into twice its bulk of water, extracted with ether, and the latter washed repeatedly with water, dried, and evaporated, and the residue purified by fractional distillation. The yields are from 85 to 95 per cent. of those theoretically possible in all cases tried, with the exception of oximes, such as that of camphor, which are very prone to undergo the Beckmann transformation.

Phenyl *iso*propyl ketone, purified in this manner, boiled at 217°, and had D_{15}^{15} 0·9886 (two specimens). (Found, C = 81·1; H = 8·2. Calc., C = 81·1; H = 8·1 per cent.)

The *semicarbazone* crystallised from alcohol in needles, melting at 181°:

0·1985 gave 0·4711 CO_2 and 0·1310 H_2O. C = 64·7; H = 7·3.

$C_{11}H_{15}ON_3$ requires C = 64·4; H = 7·3 per cent.

The oxime, purified by repeated crystallisation from light petroleum, crystallises from that solvent in transparent, lustrous, massive tablets, melting sharply at 94°. (Found, C = 73·6; H = 8·1. Calc., C = 73·6; H = 8·0 per cent.)

Rattner (*Ber.*, 1887, **20**, 206) describes the oxime as forming leaflets, melting at 58°, and Claus (*J. pr. Chem.*, 1892, [ii], **46**, 480) gives 61°.

The present authors, suspecting the possibility of stereoisomerism, have prepared the oxime in neutral solutions, in alkaline solutions of various strengths, and at temperatures varying from 15° to 100°, but in all cases the only form obtained was that melting at 94°. The oxime was only obtained in small plates or leaflets when the original ketone was contaminated with phenyl ethyl ketone, and

possibly a similar cause contributed to the results of Rattner and of Claus.

Phenyl ethyl ketoxime was prepared, for comparison with the above oxime, from phenyl ethyl ketone obtained by the interaction of magnesium ethyl bromide and benzonitrile. It had all the properties assigned to it by Pampel and Schmidt (*Ber.*, 1886, **19**, 2896).

Action of Ethyl Nitrite on Phenyl iso*Propyl Ketone in Presence of Sodium Ethoxide.*

It has been shown that certain ketones which contain the complex $\cdot CH_2\cdot CO\cdot CH<$ as part of a ring, although reacting at the $\cdot CH_2\cdot$ group when subjected to treatment with carboxylic esters in the presence of sodium ethoxide, are attacked by alkyl nitrites in similar circumstances at the $\cdot CH<$ group, ring scission taking place simultaneously probably in accordance with the following scheme (compare Clarke, Lapworth, and Wechsler, Trans., 1908, **93**, 35):

$$(1)\ R\cdot CO\cdot CHR'R'' + NO\cdot OEt = R\cdot CO\cdot C(NO)R'R'' + HOEt + NaOEt$$

$$(2)\ R\cdot CO\cdot C(NO)R'R'' + \begin{cases}2NaOH \text{ or} \\ NaOEt\end{cases} = NaO\cdot N{:}CR'R'' + \begin{cases}R\cdot CO\cdot ONa \\ R\cdot CO\cdot OEt\end{cases} + H_2O.$$

No direct proof of the formation of ester was advanced at the time, and the reaction was not applied to any simple ketone. The following experiment confirming the above scheme was carried out by the present authors with highly purified phenyl *iso*propyl ketone.

Sodium (1·5 grams) was dissolved in about 25 c.c. of 99·5 per cent. alcohol, phenyl *iso*propyl ketone (10 grams) was then added, the whole being subsequently kept cold by means of ice-water while ethyl nitrite (5 grams) in strong spirit was slowly introduced. A white solid separated almost at once, and, at the end of two hours, was collected and identified as sodium benzoate (doubtless formed as above by the action of sodium hydroxide on the nitroxylated ketone forming the intermediate product of the reaction). The alcoholic mother liquor was diluted with water, the oil which separated being removed, washed, and dried; 2 grams of pure ethyl benzoate, boiling at 212°, were obtained by fractionation of this oil.

The alkaline mother liquor was acidified and extracted with ether, which was then washed with water, dried, and evaporated; the residue was a mixture which was fractionated by means of

light petroleum. From the more soluble portion acetoxime was readily separated and identified.

Some of the cost of this investigation was defrayed from a grant from the Government Grant Fund of the Royal Society, for which the authors desire to acknowledge their indebtedness.

SCHUNCK LABORATORY, UNIVERSITY OF MANCHESTER.

CHEMISTRY DEPARTMENT, GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

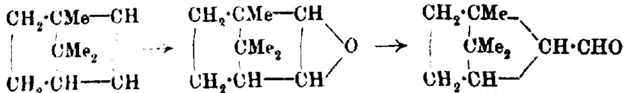
CCXIII.—*Contributions to the Chemistry of the Terpenes. Part X. The Action of Chromyl Chloride, Nitrous Acid, and Nitric Acid on Bornylene.*

By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

UP to the present time few of the derivatives of bornylene have been prepared, although the interesting relationship of this terpene to camphene, borneol, and camphor renders the full investigation of its chemical character desirable. We have accordingly begun to study these compounds, and the present paper contains an account of the results obtained by oxidising bornylene with chromyl chloride, and by attacking it with nitrous and nitric acids respectively.

Bredt and Jagelki (*Annalen*, 1900, **310**, 112) observed that camphene, on treatment with chromyl chloride, yields an additive product which reacts with water, giving as sole product camphenilanaldehyde, $C_9H_{15}\cdot CHO$. Camphenilanic acid, $C_9H_{16}\cdot CO_2H$, which is produced by spontaneous oxidation of the aldehyde, is transformed into the stereoisomeric *iso*camphenilanic acid when heated with concentrated nitric acid. Our experiments show that if bornylene is subjected to the action of chromyl chloride dissolved in carbon disulphide, it also yields a solid *additive product*, $C_{10}H_{16},2CrO_2Cl_2$, which reacts easily with water, but, unlike the corresponding camphene compound, gives two products. One of these, a saturated *chloro-ketone*, $C_{10}H_{15}OCl$, which constitutes about 65 per cent. of the whole, is apparently a derivative of camphor; the other is camphenilanaldehyde, a substance which has already been prepared from camphene in several different ways, and of which the formation from bornylene is of great interest. The aldehyde is probably mixed with a little *iso*camphenilanaldehyde, which has been obtained from camphene in a different manner (Henderson and Sutherland, this vol., p. 1539), because the acid

formed by its spontaneous oxidation in the air appears to contain a small proportion of *iso*camphenilanic acid. If, as is probable, camphenilanaldehyde has the formula given below (III), its formation from bornylene (I) must involve a certain rearrangement of the latter's molecular structure. Possibly an unstable oxide (II) is produced by the action of water on the additive compound, and at once changes to the aldehyde:



(I.) (II.) (III.)

It is most probable that camphenilanic and *iso*camphenilanic acids are stereoisomerides, and, as Bredt and Jagelki have shown, the *iso*-acid is produced when the other is subjected to prolonged heating with nitric acid, or when camphenilanaldehyde is oxidised with potassium permanganate. We have found that repeated slow crystallisations from such solvents as water, alcohol, and light petroleum likewise bring about the conversion of the one form into the other, although the process is tedious and incomplete; quite a number of different mixtures of the two acids which have constant melting points can be obtained by rapid crystallisation. From acetic acid, on the other hand, camphenilanic acid can be crystallised several times with little or no formation of the *iso*-acid. We have also observed that on treatment with semicarbazide hydrochloride and potassium acetate in the usual manner, camphenilanaldehyde yields the semicarbazone of *iso*camphenilanaldehyde, which, when liberated by the action of dilute acids, is converted into the *iso*-acid on exposure to the air.

For comparison with bromocamphenilanic acid, we prepared *bromo*iso*camphenilanic acid*, $C_9H_{14}Br{\cdot}CO_2H$, by converting the *iso*-acid into its *chloride*, $C_9H_{15}{\cdot}COCl$, heating this compound with bromine under pressure at about 60°, and decomposing the product, the *chloride* of bromo*iso*camphenilanic acid, $C_9H_{14}Br{\cdot}COCl$, with water. If the bromination of the chloride is carried out at a higher temperature, a crystalline neutral compound, which appears to have the formula $C_{10}H_{15}OBr$, is produced along with the bromo-acid. On one occasion we used *iso*camphenilanic acid mixed with a considerable proportion of camphenilanic acid, in the expectation of obtaining a mixture of the bromo-acids which might be more easily separated than the parent substances. The sole product, however, was bromo*iso*camphenilanic acid, and it is evident that during the process the chloride of camphenilanic or of bromocamphenilanic acid must have undergone conversion into the corresponding derivative of *iso*camphenilanic acid.

When heated with aqueous sodium carbonate, bromocamphenilanic acid yields the α-hydroxy-acid, camphenylic acid,

$$C_9H_{14}(OH)\cdot CO_2H,$$

but bromo*iso*camphenilanic acid behaves quite differently, being converted into an unsaturated acid, $C_9H_{13}\cdot CO_2H$.

The chloro-ketone, $C_{10}H_{15}OCl$, forms a *semicarbazone*, which melts and decomposes at 234—235°. The chlorine in the ketone is not easily displaced, but on heating the compound with concentrated alcoholic potassium hydroxide under pressure at 160° it is converted into camphor, and it is slowly oxidised to camphoric acid by treatment with an alkaline solution of potassium permanganate. The compound, therefore, is a *chlorocamphor*, and possibly is stereoisomeric with 3-chlorocamphor,

$$\begin{array}{l} CH_2\cdot CMe-CO \\ \mid \quad\ \ \mid \qquad\ \ \mid \\ \mid \quad CMe_2 \quad \mid \\ \mid \quad\ \ \mid \qquad\ \ \mid \\ CH_2\cdot CH-CHCl \end{array}$$

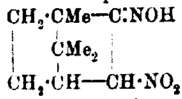
, which melts at 93—94°.

The formation of camphenilanaldehyde, a derivative of camphene, from bornylene is of considerable importance, as indicating that there is great similarity between the nuclei of these terpenes. The results of the investigation of other derivatives of these terpenes, which we hope to be able to communicate to the Society before long, appear to support this view.

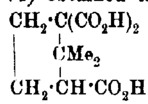
Results which are of importance as regards the question of its constitution have been obtained by subjecting camphene to the action of nitrous and nitric acids, and it therefore appeared of interest to investigate the behaviour of bornylene when attacked by these reagents. From camphene, by treatment with nitrous acid, Jagelki (*Ber.*, 1899, **32**, 1498) obtained a crystalline nitronitrosite, $C_{10}H_{15}(NO_2)(N_2O_3)$, and an oily *iso*nitrosite, $C_{10}H_{16}(N_2O_3)$, which was readily decomposed, yielding the so-called camphenil nitrite, $C_{10}H_{15}\cdot NO_2$; the latter compound was easily converted into camphenilanaldehyde, $C_{10}H_{16}O$, and camphenilone, $C_9H_{14}O$, respectively. When treated in a similar manner with nitrous acid, bornylene has been found to yield several different compounds, some of which differ essentially in character from the derivatives obtained from camphene. The chief product was a crystalline *nitrosite*, $C_{10}H_{16}(N_2O_3)$, which proved to be bimolecular, and evidently has the same nucleus as bornylene, because it yields camphoric acid on oxidation:

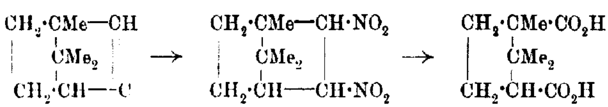
$$\begin{array}{l} CH_2\cdot CMe-CH \\ \mid \quad\ \ \mid \qquad \| \\ \mid \quad CMe_2 \ \| \\ \mid \quad\ \ \mid \qquad \| \\ CH_2\cdot CH-CH \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CMe-CH\cdot NO \\ \mid \quad\ \ \mid \qquad \mid \\ \mid \quad CMe_2 \ \mid \\ \mid \quad\ \ \mid \qquad \mid \\ CH_2\cdot CH-CH\cdot NO_2 \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CMe\cdot CO_2H \\ \mid \quad\ \ \mid \\ \mid \quad CMe_2 \\ \mid \quad\ \ \mid \\ CH_2\cdot CH\cdot CO_2H \end{array}$$

Another product was a viscous liquid of a green colour, which

owing to its extreme instability could not be purified sufficiently for analysis. It is very similar in properties to the *iso*nitrosite prepared from camphene, for example, in its solubility in aqueous solutions of alkali hydroxides, and in all probability is the corresponding *bornylene isonitrosite*, 

In addition to the above, we found among the products of the reaction a considerable quantity of a crystalline solid, melting at 198°, which was proved to be camphorquinone, and a very small amount of a colourless, crystalline compound, which melted at 84—85°. This substance contains nitrogen, but the quantity in our hands was too small to permit of its identification.

On oxidising camphene with nitric acid, Marsh and Gardner (Trans., 1891, **59**, 648; 1896, **69**, 74) obtained the tribasic camphoic (carboxy*apo*camphoric) acid, . When bornylene was oxidised in a similar manner, we found, as was to be expected, that the chief product was camphoric acid. Along with this there separated from the mixture of oxidation products a yellow, crystalline compound, which melts at 137°, and volatilises in a current of steam. This compound proved to be a *dinitrocamphane*, $C_{10}H_{16}(NO_2)_2$, and its formation must be due to the addition of nitric peroxide, produced by reduction of the nitric acid, to some of the bornylene. On oxidation with dilute alkaline permanganate, it is readily converted into camphoric acid:



On reduction with sodium and alcohol, or with tin and hydrochloric acid, this dinitrocamphane is completely decomposed, but alcoholic ammonium sulphide converts it into a yellow, crystalline substance, which is apparently not an amino-derivative, but possibly a mononitrocamphane.

Besides these substances the mixture of products was found to contain a very small quantity of a colourless, crystalline compound, which melts at about 174°. This compound, which contains nitrogen, is neutral in character.

Our results show that neither nitrous nor nitric acid, when used under the conditions described below, tends to bring about any

rearrangement of the nucleus of bornylene, for the products are all typical derivatives of that hydrocarbon, and not of camphene.

We are at present engaged in studying other derivatives of bornylene, and shall submit our results to the Society before long.

EXPERIMENTAL.

The Oxidation of Bornylene with Chromyl Chloride.

Preparation and Oxidation of Bornylene.—Bornylene was prepared from borneol, through bornyl methyl xanthate, essentially according to the method of Tschugaeff (*Ber.*, 1899, **32**, 3332), but with modifications which experience has shown to be of value. In the first stage of the process the best results were obtained by boiling a solution of 200 grams of borneol in 250 grams of dry toluene with the necessary quantity of sodium. The heating of the liquid was effected by means of a glycerol bath, because when a sand-tray is used, local overheating and consequent charring through decomposition of the material are apt to occur, and there is considerable risk of the flask breaking.

A 10 per cent. solution of 100 grams of chromyl chloride (2 mols.) in dry carbon disulphide was slowly added, in small portions, to a well-cooled solution of 44 grams of bornylene (1 mol.) in the same solvent and of similar concentration, with thorough agitation after each addition. The reaction proceeded smoothly, with evolution of heat, and a dark brown precipitate slowly settled, and was then collected, washed with carbon disulphide, and transferred to wide-mouthed bottles while still in the form of a pasty mixture with some of the solvent. The mass was added, in small quantities at a time, to ice-cold water containing a little sulphurous acid, and the mixture vigorously shaken after each addition until the solid was completely decomposed, with the result that an oily substance separated from the aqueous solution. The oxidation product was extracted by repeated agitation of the mixture with carbon disulphide, and the extract was well washed with water, dried with calcium chloride, and heated to expel the carbon disulphide. The yield is very good, little or no resinification taking place.

The *additive compound*, $C_{10}H_{16},2CrO_2Cl_2$, thus obtained from bornylene is, when in the dry state, a light brown powder. It is extremely hygroscopic, and decomposes on exposure to moist air, forming a dark green liquid with a sweet odour.

Separation and Identification of Camphenilanaldehyde.—The oily liquid obtained from the additive product was well mixed with a saturated solution of sodium hydrogen sulphite, with the result that after some time a crystalline "bisulphite compound" separated in

very small, colourless plates. Ether was added in order to extract the substance which had not reacted with the bisulphite, and the ethereal solution was separated and treated with fresh quantities of the reagent until no more of the bisulphite compound was formed. The crystals were collected, and washed with alcohol and with ether, and the aqueous filtrate was extracted with ether, this ethereal solution being added to the first. The bisulphite compound was mixed with aqueous sodium carbonate, and heated with steam, and the aldehyde which solidified in the receiver was collected, quickly dried by pressure in porous paper, and distilled in an atmosphere of dry carbon dioxide. In this way the aldehyde was obtained in colourless crystals, with a strong odour. It melted at 71—72°, boiled at 192—193° under atmospheric pressure, and was quickly oxidised on exposure to the air. Its semicarbazone was prepared, and purified by crystallisation from methyl alcohol, from which it separated in lustrous, pearly leaflets, with the melting point 191—192°. (Found, C=63·1; H=9·1; N=20·3. Calc., C=63·1; H=9·1; N=20·1 per cent.)

As the properties of this aldehyde from bornylene appeared to be identical with those of Bredt's camphenilanaldehyde, we prepared a quantity of the latter from camphene for purposes of comparison, and converted some of it into its semicarbazone. (Found, N=20·2.)

This semicarbazone melted at the same temperature as that prepared from the aldehyde obtained from bornylene, and the melting point remained unaltered when the two compounds were mixed. In short, bornylene, when oxidised with chromyl chloride, yields the same aldehyde as camphene does when similarly treated.

We observed also that the semicarbazones prepared from camphenilan- and *iso*camphenilan-aldehydes, as also a mixture of the two, have the same melting point. To clear up this point we decomposed some of the semicarbazone prepared from camphenilanaldehyde by warming it with the calculated quantity of dilute sulphuric acid, and found that the liberated aldehyde was wholly oxidised to *iso*camphenilanic acid on exposure to the air. Hence it appears that the product of the action of semicarbazide hydrochloride on camphenilanaldehyde is the semicarbazone of *iso*camphenilanaldehyde—a result which is not surprising, because the two aldehydes are almost certainly stereoisomerides.

Camphenilanic and iso*Camphenilanic Acids.*—The aldehyde obtained from bornylene was exposed to the air for some time, and, after oxidation appeared to be complete, the acid formed was separated from any unchanged aldehyde by means of aqueous sodium carbonate. Acidification of the alkaline solution produced an oily precipitate, which soon solidified, and was then collected,

washed with water, and dried. A melting-point determination showed that, whilst the bulk of the product was camphenilanic acid, a small proportion of an acid of higher melting point was also present. By fractional crystallisation from somewhat diluted acetic acid the camphenilanic acid was obtained in crystals melting at 65°; the other acid separated from light petroleum or from dilute alcohol in colourless prisms, which melted at 118°, and in all other respects was exactly similar to *iso*camphenilanic acid. Analysis established its identity. (Found, C = 71·6; H = 9·3. Calc., C = 71·4; H = 9·5 per cent.)

Having accumulated a quantity of camphenilanic acid, we endeavoured to convert it into its isomeride by crystallisation from different solvents, and found that when repeatedly crystallised from water, alcohol, or light petroleum, camphenilanic acid is gradually transformed into *iso*camphenilanic acid. For example, a specimen of the former acid which melted at 65°, after one crystallisation from water melted at 70°, and after a second at 86°. The process is tedious and unsatisfactory owing to the tendency of the two acids to form mixtures of constant melting point, and the consequent difficulty in separating them. *iso*Camphenilanic acid is not formed when camphenilanic acid is crystallised from glacial acetic acid, or heated at a temperature above its melting point for several days, or exposed to ultra-violet light. Bredt showed that the *iso*-acid is produced when camphenilanic acid is boiled with concentrated nitric acid, but according to our experience some of the latter remains unaltered, even when the heating is prolonged for a fortnight. A mixture of the two acids was also obtained when camphenilanaldehyde was oxidised with an alkaline solution of potassium permanganate. A comparatively simple method of obtaining *iso*camphenilanic acid is to convert camphenilanaldehyde into the semicarbazone, to decompose this compound with dilute acids, and to allow the *iso*camphenilanaldehyde thus produced to undergo oxidation in the air.

*Preparation of Bromo*iso*camphenilanic Acid and of the Unsaturated Acid* $C_9H_{13}{\cdot}CO_2H$.—The *chloride* of iso*camphenilanic acid*, $C_9H_{15}{\cdot}COCl$, was prepared by adding the acid in small portions to a mixture of the calculated quantity of phosphorus pentachloride with light petroleum, heating under a reflux condenser until the reaction was completed, and finally distilling fractionally under diminished pressure. The chloride is a colourless, oily liquid, with a not unpleasant odour, which boils at 118°/25 mm., and rapidly decomposes in moist air, with formation of *iso*camphenilanic acid. By heating in a sealed tube for several hours at about 60° with a slight excess of bromine it was converted into the *chloride* of *bromo-*

isocamphenilanic acid, $C_9H_{14}Br \cdot COCl$, which is also a heavy, viscous liquid, and is decomposed by water, giving *bromoisocamphenilanic acid*, $C_9H_{14}Br \cdot CO_2H$. The chloride was poured into water, and the mixture well stirred until the oily chloride was completely converted into the crystalline acid, which was collected, washed with water, and purified by recrystallisation, first from dilute methyl alcohol, and finally from light petroleum. The acid forms small, colourless prisms, which melt at 204—205°. It is readily soluble in alcohol, ether, or light petroleum, but almost insoluble in water:

0·2022 gave 0·1550 AgBr. Br = 32·6.

$C_{10}H_{15}O_2Br$ requires Br = 32·3 per cent.

In the first preparation of bromo*iso*camphenilanyl chloride the mixture was heated in a sealed tube at 100° for about twenty-four hours. On treatment of the product with water, a mixture of bromo*iso*camphenilanic acid with a considerable proportion of a neutral compound, $C_{10}H_{15}OBr$, was obtained. This substance crystallises from methyl alcohol in minute, colourless needles, which melt at 182°. It is sparingly soluble in methyl alcohol, readily so in ether or light petroleum, and insoluble in water and in aqueous solutions of sodium carbonate or sodium hydroxide:

0·2076 gave 0·1687 AgBr. Br = 34·6.

$C_{10}H_{15}OBr$ requires Br = 34·6 per cent.

With the object of preparing the corresponding hydroxy-derivative, bromo*iso*camphenilanic acid was warmed for about three hours on the water-bath with aqueous sodium carbonate. From the solution, on cooling, a rather sparingly soluble sodium salt crystallised out. The salt was dissolved in water and decomposed by addition of dilute sulphuric acid, and the precipitated acid was purified by crystallisation from dilute methyl alcohol. Examination of this substance proved it to be, not the expected hydroxy-acid, but an unsaturated *acid* of the formula $C_9H_{13} \cdot CO_2H$. It crystallises in fine, lustrous plates, melts at 147°, is readily soluble in alcohol or ether, but insoluble in water, and volatilises in a current of steam. It immediately reduces an alkaline solution of potassium permanganate in the cold:

0·1855 gave 0·4878 CO_2 and 0·1480 H_2O. C = 71·7; H = 8·8.

$C_{10}H_{14}O_2$ requires C = 72·2; H = 8·4 per cent.

The *sodium* salt, $C_9H_{13} \cdot CO_2Na$, separates from water, in which it is not very readily soluble, in beautiful, silky plates.

Separation of the Chloro-ketone, $C_{10}H_{15}OCl$.—The ethereal solution of the oxidation product, from which the aldehyde had been removed by treatment with sodium hydrogen sulphite, was washed successively with aqueous sodium carbonate and with water, and

dried. The ether was removed by distillation, the residue heated in a current of steam, and the yellow solid, which condensed in the receiver, collected and pressed on a porous plate to remove traces of oily matter. Purification of this substance by crystallisation was difficult, owing to its great solubility in all the usual organic solvents, and the method finally adopted was repeated fractional precipitation with water from a solution in glacial acetic acid. Once partly purified in this way the substance can be crystallised from dilute alcohol. When pure it forms minute, colourless crystals, which melt sharply at 165°, and have a faint, pleasant odour. It is extremely volatile in steam, but decomposes on distillation, even under diminished pressure. Its solubility in organic solvents is very great, but it is insoluble in water. It has the character of a saturated ketone, readily forming a semicarbazone, but resisting oxidation:

0·2218 gave 0·5230 CO_2 and 0·1610 H_2O. C = 64·3; H = 8·1.
0·1636 „ 0·1256 AgCl. Cl = 19·0.

$C_{10}H_{15}OCl$ requires C = 64·3; H = 8·1; Cl = 19·0 per cent.

The *semicarbazone* of the *chloro-ketone*,

$$C_{10}H_{15}Cl{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2,$$

which was prepared in the usual way, crystallises from dilute alcohol in small, colourless prisms. It is fairly readily soluble in alcohol, and melts at 234—235°, beginning to decompose a little below this temperature:

0·1850 gave 28·6 c.c. N_2 (moist) at 14° and 758 mm. N = 18·2.

$C_{11}H_{18}ON_3Cl$ requires N = 17·3 per cent.

The chloro-ketone was found to be slowly oxidised by potassium permanganate in alkaline solution. After heating on the water-bath for two days, the excess of permanganate was reduced with sulphurous acid, the precipitated manganese dioxide removed by filtration, and the filtrate concentrated to small bulk. On addition of dilute sulphuric acid a crystalline acid was obtained, and was collected and recrystallised from hot water. The purified acid melted at 187°, and in other respects resembled camphoric acid. Its identity was established by heating it at a temperature above its melting point in a current of carbon dioxide, distilling the product, and recrystallising the distillate from alcohol. The crystals melted sharply at 221°, the melting point of camphoric anhydride.

The removal of chlorine from the ketone was difficult, and attempts to effect this by heating it with silver oxide in alcoholic solution and by treatment with sodium and alcohol proved fruitless. The end was attained by heating 5 grams of the ketone with a concentrated alcoholic solution of 2 grams of potassium hydroxide in a sealed tube for seven hours at 150—160°. The alcoholic

solution was mixed with water and agitated several times with ether, and the ethereal extract was washed with water, dried, and distilled to remove the ether. The residue was heated in a current of steam, and a crystalline solid separated from the distillate, which in all respects was indistinguishable from camphor. The solid was converted into a semicarbazone, which after crystallisation from methyl alcohol melted at 236°, the melting point of camphorsemicarbazone, and from which, by treatment with dilute sulphuric acid, a specimen of camphor, melting at 174°, was regenerated.

From these results it is evident that the chloro-ketone is a *chlorocamphor*, different from any hitherto described.

The Action of Nitrous Acid on Bornylene.

Preparation of the Nitrosite.—Glacial acetic acid was added very slowly, in small quantities at a time, to a concentrated aqueous solution of 100 grams of sodium nitrite, on which rested a concentrated solution of 100 grams of bornylene in light petroleum. The mixture was gently warmed on the water-bath under a reflux condenser, with occasional agitation, for about an hour, and then left for twenty-four hours at the ordinary temperature. During this time crystals of the nitrosite slowly separated at the surface of the aqueous layer, the light petroleum acquiring, first a blue, then an intense green, and finally, at the end of the reaction, a yellow coloration. The petroleum solution was removed, and repeatedly treated in the same manner with fresh quantities of sodium nitrite and acetic acid until the odour of bornylene had disappeared. This method gave better results than prolonged treatment of bornylene with nitrous acid in one operation. The crystals of the nitrosite were separated from the aqueous solution by filtration through glass wool, thoroughly washed with water, alcohol, and ether successively, and purified by crystallisation from acetone. From this solvent the nitrosite separates in beautiful, silky needles, which, when quickly heated, melt sharply at 163°, forming a bluish-green liquid, which decomposes with violent gas evolution. It is readily soluble in acetone, glacial acetic acid, benzene, or chloroform, but very sparingly so in alcohol or ether, and is insoluble in water or aqueous solutions of alkali hydroxides or hydrochloric acid. The solutions have a characteristic blue colour. The nitrosite is not decomposed by alkali hydroxides or concentrated hydrochloric acid, even when heated:

0·2044 gave 0·4176 CO_2 and 0·1470 H_2O. C=55·7; H=8·0.

0·2055 ,, 24 c.c. N_2 (moist) at 13·2° and 740 mm. N=13·4.

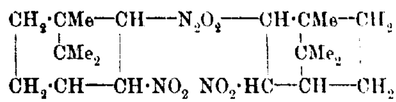
$C_{10}H_{16}O_3N_2$ requires C=56·6; H=7·5; N=13·2 per cent.

Determinations of the molecular weight by the ebullioscopic method in acetone solution gave the following results:

Substance (gram).	Solvent (grams).	*E.*	M.W.
0·2196	17·47	0·05°	432
0·4291	17·47	0·118°	358
0·6495	17·47	0·185°	346

$C_{10}H_{16}O_3N_2$ requires M.W. = 212.

These results indicate that the substance is bimolecular, the fall in the molecular weight in the later determinations being possibly due to a slight decomposition of the complex molecule on continued heating of the solution. The bimolecular form may be represented thus:



The nitrosite, on oxidation with a warm dilute alkaline solution of potassium permanganate, yields an acid, which melts at 187°, and in all other respects is identical with camphoric acid.

Separation of the iso*Nitrosite.*—The light petroleum, from which the nitrosite had separated, was repeatedly agitated with concentrated aqueous potassium hydroxide until nothing more passed into solution, and the red alkaline liquid was diluted with water and acidified with hydrochloric acid, care being taken to keep the mixture cool. The liquid was repeatedly agitated with ether, the ethereal extract washed with water and dried, and, after removal of the ether by distillation, the iso*nitrosite* was obtained as a viscid, oily liquid, with a green colour and a pleasant odour. It is an extremely unstable substance, decomposing with violent evolution of gas when heated, even under greatly diminished pressure. It dissolves in aqueous solutions of alkali hydroxides, and the alkali derivatives are extremely readily soluble in all solvents. A small quantity of the *potassium* salt, probably $C_{10}H_{15}\cdot N_2O_3K$, was obtained as an orange-coloured powder by the action of potassium ethoxide on a solution of the *iso*nitrosite in dry benzene. Attempts to prepare products of hydrolysis and of reduction of the *iso*nitrosite were unsuccessful, as in each case the substance was apparently completely decomposed; yet its close resemblance to the corresponding *iso*nitrosite prepared from camphene lends probability to the conclusion that this compound is bornylene *iso*nitrosite.

Separation of Camphorquinone.—After extraction of the *iso*nitrosite by aqueous potassium hydroxide, the petroleum solution was well washed with water, dried, and, after removal of the light petroleum by distillation, the residual yellow oil was fractionated

under diminished pressure. The most volatile fraction consisted of some bornylene which had escaped attack, and the second fraction, which was small in quantity, had a strong odour of camphor; the last fraction, which had a deep yellow colour, deposited some crystals on keeping. After removal of these crystals, the yellow, oily liquid which remained was placed in the ice-chest, when it gradually solidified, and after purification by crystallisation from light petroleum was obtained in delicate needles, of a deep yellow colour and with a strong odour, which melted sharply at 197—198°. It is readily soluble in organic solvents, and sparingly so in hot water; it volatilises very easily in a current of steam, and sublimes readily at a low temperature. In all these respects it is identical with camphorquinone. The aqueous solution, from which the crystals of nitrosite had been separated by filtration, had a deep yellow colour, and also yielded some camphorquinone.

The crystalline solid, which separated from the distillate of crude camphorquinone, melted at 70—80°, and was evidently a mixture of the latter with some other substance. By repeated crystallisation of this mixture from methyl alcohol this compound was obtained in colourless prisms, which melted at 84—85°. It is sparingly soluble in water, and readily so in organic solvents. Analysis gave results which indicated that the substance might be bornylene nitrite, but we were unable, from lack of material, to confirm this. On treatment with alkali it yields a substance which resembles camphor:

0·1984 gave 0·4866 CO_2 and 0·1774 H_2O. C=66·9; H=9·9.
0·1472 „ 9·95 c.c. N_2 (moist) at 24° and 777 mm. N=7·7.
$C_{10}H_{15}O_2N$ requires C=66·2; H=8·3; N=7·7 per cent.

The Action of Nitric Acid on Bornylene.

Separation of Dinitrocamphane.—Forty grams of bornylene were warmed on the water-bath under a reflux condenser with about 500 c.c. of 30 per cent. nitric acid. Vigorous action took place, nitrous fumes being evolved in quantity, whilst owing to the heat of the reaction some of the unattacked bornylene volatilised into the tube of the condenser. After about an hour, when the first action had ceased, the flask and its contents were allowed to cool, and a further quantity of 270 c.c. of nitric acid (D 1·4) was added very gradually in small portions at a time. Care must be taken at this stage, for if too much of the strong acid was added at once oxidation took place with almost explosive violence. During this part of the process the bornylene which had volatilised was attacked by the nitric acid and the nitrous fumes, and washed back

into the flask. After all visible action had ceased, the solution was boiled in order to expel nitrous fumes, and left for twelve hours at the ordinary temperature, when a mass of crystals was deposited. The crystals were separated from the strongly acid liquid by filtration through glass wool, well washed with water, and dried in porous paper. Inspection revealed the presence of two substances in the product, some of the crystals being yellow and others colourless. The colourless crystals were found to be soluble in aqueous sodium carbonate, and therefore the mixture was warmed with excess of this reagent and the alkaline solution repeatedly shaken with ether, in which the yellow substance dissolved. The ethereal solution was washed with water, dried, and, after removal of the ether by distillation, a yellow, oily substance was obtained, which became crystalline on keeping. After purification by crystallisation from methyl alcohol, this substance, 1:2-*dinitrocamphane*, had the form of long, slender, pale yellow needles, which melted at 137° without any signs of decomposition. It is readily soluble in ether or chloroform, moderately so in methyl or ethyl alcohol, and insoluble in water or acids. It dissolves to a small extent in hot solutions of the alkali hydroxides, imparting a deep yellow colour to the liquid. It volatilises slowly in a current of steam. Towards bromine or potassium permanganate the compound is inactive, being evidently saturated. The yield was about 5 per cent. of the bornylene taken. Analysis showed that it had the composition of a dinitrocamphane:

0·2033 gave 0·3916 CO_2 and 0·1320 H_2O. C = 52·6; H = 7·2.

0·2363 ,, 26·4 c.c. N_2 (moist) at 16° and 737 mm. N = 12·4.

$C_{10}H_{16}O_4N_2$ requires C = 52·6; H = 7·0; N = 12·3 per cent.

When warmed with a dilute alkaline solution of potassium permanganate, the yellow crystals of the dinitrocamphane were gradually oxidised, and passed into solution. After the oxidation was completed, the precipitated manganese dioxide was removed by filtration, the filtrate acidified, and the acid which separated collected and crystallised from boiling water. It then melted at 187°, and was proved to be camphoric acid by conversion into camphoric anhydride, melting at 221°.

The ready oxidation of the substance to camphoric acid, and the results of analysis, prove that it has the bornylene or camphane structure, and is in all probability a dinitrocamphane, but attempts to prepare the corresponding diamino-derivative were unsuccessful. When sodium and alcohol or tin and hydrochloric acid were used as the reducing agent, complete disintegration of the molecule took place, gaseous fatty amines being evolved, and no definite product was obtained. Reduction with ammonium sulphide, on the other

hand, yielded a well-characterised compound. The dinitrocamphane was dissolved in alcohol, the necessary quantity of a concentrated solution of ammonia added, and hydrogen sulphide passed into the solution for some time. During this operation the liquid, previously almost colourless, acquired a dark red colour. The solution was then boiled for half an hour, filtered to remove precipitated sulphur, and left to cool, when crystals of a deep yellow colour separated. After recrystallisation from alcohol, the new compound was obtained in minute, hard prisms of a canary-yellow colour, which melt at 196—198°. It is only sparingly soluble in alcohol, and insoluble in water, but dissolves readily in ether. The quantity at our disposal only permitted of a nitrogen estimation. The result suggested that the new compound may be a mononitrocamphane, but it remains to be proved whether or not this is the case:

0·2026 gave 13·5 c.c. N_2 (moist) at 19° and 763 mm. N = 7·7.

$C_{10}H_{17}O_2N$ requires N = 7·6 per cent.

Separation of Camphoric Acid.—As already stated, colourless crystals of an acid separated along with the dinitrocamphane from the acid solution in which the bornylene had been oxidised, and were removed by treatment of the mixture with aqueous sodium carbonate. A further quantity was obtained from the acid mother-liquor, which was subjected to steam distillation in order to remove a little dinitrocamphane which remained in solution, rendered alkaline by addition of excess of sodium carbonate, and agitated with ether, which dissolved a little of a substance which separated when the acid was neutralised. The mixed alkaline solutions were concentrated, and on acidification yielded a large quantity of an acid. After recrystallisation from water the acid melted at 187°, and its identity with camphoric acid was proved by analysis. (Found, C = 60·2; H = 8·1. Calc., C = 60·0; H = 8·0 per cent.)

The ethereal solution of the substance extracted from the alkaline liquid was washed and dried, and after removal of the ether a viscous, oily substance remained. This was distilled under diminished pressure in an atmosphere of dry carbon dioxide; considerable decomposition took place, but a portion which distilled at 180—185°/25 mm. solidified on cooling to a yellow mass. After repeated crystallisation from light petroleum the compound was obtained in the form of minute, colourless needles, which melted at about 174°. It is very readily soluble in alcohol, ether, or acetone, somewhat sparingly so in light petroleum, and insoluble in water, alkalis, or dilute mineral acids. The yield of this compound is extremely small, and from several different preparations only enough for one analysis was obtained, according to which the compound contains C = 71, H = 10, and N = 6·7 per cent.

We take this opportunity of thanking Mr. D. S. Dawson, B.Sc., and Mr. William Caw for valuable assistance, and the Carnegie Trust for a grant in aid of the expense of this work.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CCXIV.—*The Constitution of Camphene.*

By GEORGE GERALD HENDERSON and ISIDOR MORRIS HEILBRON.

THERE is still room for difference of opinion regarding the constitution of camphene, but this at least is certain, that the formula originally assigned to this terpene by Bredt is in reality that of the closely related bornylene (I), as is shown by the formation of the latter from borneol (II) through bornyl methyl xanthate, and by the ease with which it is converted into camphoric acid by oxidation. There can also be little doubt that the nuclei of camphene and bornylene, although to a large extent similar in structure, differ from one another more widely than, for example, in the position of a double linking, because, among other reasons, it has been observed that, on reduction by the contact method of Sabatier and Senderens, bornylene readily yields camphane, whilst camphene is converted into a dihydro-derivative which is quite different from camphane (Henderson and Pollock, Trans., 1910, **97**, 1620). It is generally agreed that bornylene is the normal product from borneol, and therefore that the formation of camphene from this alcohol is attended by a certain structural rearrangement.

From camphene, by the action of chromyl chloride, Bredt and Jagelki (*Annalen*, 1900, **310**, 112) obtained an additive compound which on treatment with water gave only one product, camphenilanaldehyde (V). From the corresponding acid an α-hydroxy-derivative, camphenylic acid (VI), was prepared, and from the latter, by oxidation, the ketone camphenilone (VII), which so closely resembles camphor both in physical and in physiological properties. By means of an entirely different oxidising agent, hydrogen peroxide, Henderson and Sutherland (this vol., p. 1539) recently obtained from camphene a mixture of oxidation products, the chief of which were *iso*camphenilanaldehyde (which is almost certainly a stereoisomeride of camphenilanaldehyde), camphenilone, and an acid, $C_{10}H_{16}O_2$, isomeric with *iso*camphenilanic acid, into which it is transformed when heated with acetic anhydride. Camphene has also been converted into camphenilanaldehyde or camphenilone respec-

tively in other direct and simple ways; thus, when camphene nitrite (VIII) is hydrolysed, it yields the aldehyde, through rearrangement of the unsaturated alcohol (IX), which is the direct product of hydrolysis, while camphenilone is produced when the nitrite is treated with a dilute solution of potassium permanganate (Jagelki, *Ber.*, 1899, **32**, 1498). Further, in the course of an elaborate investigation of the products obtained by oxidising camphene with a dilute aqueous solution of potassium permanganate, Moycho and Zienkowski (*Annalen*, 1905, **340**, 17) prepared camphene glycol (IV) in considerable quantity, and showed that this compound must contain two hydroxyl groups, although it only yields a monobenzoate, and that all its reactions point to the formula,

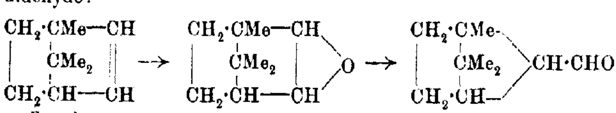
$$C_8H_{14}\!:\!C(OH)\cdot CH_2\cdot OH.$$

They found that camphenilanaldehyde was formed from the glycol under such conditions that no structural rearrangement would take place, and therefore that the linking of the carbon atoms in the two compounds is the same. Camphenylic acid and camphenilone were identified among the other products of the oxidation of the camphene, and were also prepared from the pure glycol by treatment with permanganate. Moycho and Zienkowski consider that their results prove conclusively the presence of the group $>C\!:\!CH_2$ in the molecule of camphene, and this view is supported by the observation of Balbiano and Paolini (*Ber.*, 1903, **36**, 3375) that camphene yields an additive compound when treated with aqueous mercuric acetate, whereas, according to these observers, the presence of a $\cdot CH\!:\!CH\cdot$ group would lead to the formation of an oxidation product.

The formation of camphenilanaldehyde from camphene by such different methods as those quoted, indicates that the central nucleus and the mode of attachment of the side groups in each of the two substances are identical. Definite proof of this has been given by Semmler (*Ber.*, 1909, **42**, 246, 962), who converted the aldehyde into an *enol*-acetate, reduced the latter to camphenilyl alcohol, prepared the corresponding chloride, and from this, by treatment with sodium and alcohol, regenerated camphene. It is also known that camphenilone has the same nucleus as camphene, for not only is it produced when the hydrocarbon is oxidised with potassium permanganate, or with hydrogen peroxide, or with moist ozone, but, in addition, the direct synthesis of camphene from camphenilone, through methylcamphenilol, has been effected by Moycho and Zienkowski (*Ber.*, 1905, **38**, 1061).

The formation and relationships of the derivatives mentioned above can be explained if the constitution of camphene be repre-

sented by the formula $\begin{array}{l} CH_2\cdot CH-CMe_2 \\ \quad\; CH_2 \\ CH_2\cdot CH-C{:}CH_2 \end{array}$. This formula was suggested by Wagner as the result of his study of the alcohols borneol and *iso*borneol, which, as corresponding with bornylene and camphene respectively, were believed to have quite different structures. But although borneol is a secondary, and *iso*borneol apparently a tertiary alcohol, it seems difficult to reconcile the view that their nuclei are entirely different with the facts that *iso*borneol on oxidation yields camphor, a ketone with the same nucleus as borneol, that under suitable conditions camphene can be obtained from borneol, and that *iso*borneol is converted into the sodium derivative of borneol when heated with sodium in xylene solution. If camphene had the constitution expressed in Wagner's formula, or in the formula $\begin{array}{l} CH_2\cdot CH-CMe_2 \\ \quad\; CH_2 \;\; CH \\ CH_2\cdot CH-CH \end{array}$, which has been tentatively proposed by Aschan in a recent paper (*Annalen*, 1910, **375**, 336), its formation from borneol would involve a greater rearrangement of the molecule than seems probable from the facts already quoted, and, moreover, observations recently made in this laboratory (Henderson and Heilbron, this vol., p. 1887) indicate that the molecular structure of camphene is closely related to that of bornylene. It has been found that, on treatment with chromyl chloride, bornylene gives an additive product, from which, by the action of water, excellent yields of two substances are obtained. One of these, a chloro-ketone of the formula $C_{10}H_{15}OCl$, appears to be a chlorocamphor, while the other is a derivative of camphene, being, in fact, camphenilanaldehyde. If the formula of the aldehyde is that given below, the formation of this camphene derivative from bornylene can be easily understood, for it is only necessary to assume that when the additive compound reacts with water a substance of the type of an oxide is formed, which by a slight rearrangement passes into the aldehyde:



Bornylene. Camphenilanaldehyde.

Such a rearrangement of the bornylene molecule is insignificant compared with that which would be involved if camphene were constituted as represented in the formulæ of Wagner or of Aschan.

These results lead to the conclusion that as regards the greater part of their respective molecules, namely, the residue,

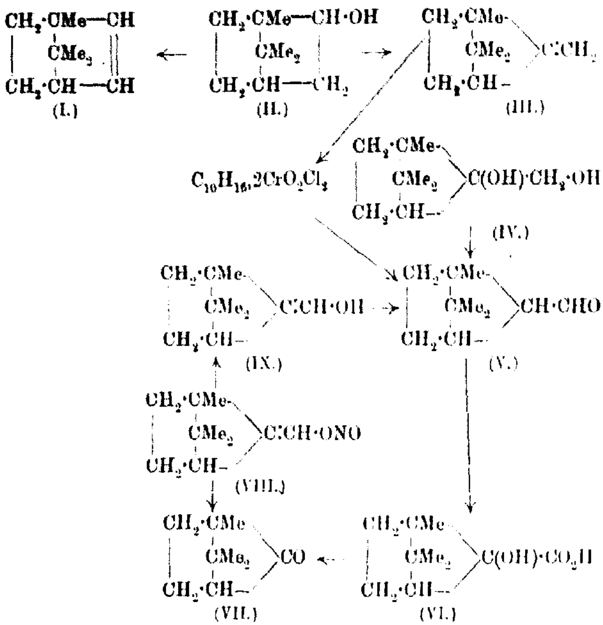
$$\begin{array}{l} CH_2\cdot CMe\cdot \\ | \quad\;\; | \\ | \quad\;\; CMe_2, \\ | \quad\;\; | \\ CH_2\cdot CH\cdot \end{array}$$

camphene and bornylene are identical. Support is given to this conclusion by the fact that camphene resembles bornyl chloride, which also contains this residue, in yielding camphor on oxidation with chromate mixture, and also, to a less extent, by the observation of Marsh and Gardner (Trans., 1891, **59**, 648; 1896, **69**, 74) that camphene is oxidised by moderately dilute nitric acid to camphoic (carboxy*apo*camphoric) acid, which on heating loses carbon dioxide and forms *apo*camphoric acid, which has been synthesised by Komppa (*Ber.*, 1901, **34**, 2472):

$$\begin{array}{l} CH_2\cdot C(CO_2H)_2 \\ | \quad\;\; | \\ | \quad\;\; CMe_2 \\ | \quad\;\; | \\ CH_2\cdot CH\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} CH_2\cdot CH\cdot CO_2H \\ | \quad\;\; | \\ | \quad\;\; CMe_2 \\ | \quad\;\; | \\ CH_2\cdot CH\cdot CO_2H \end{array}.$$

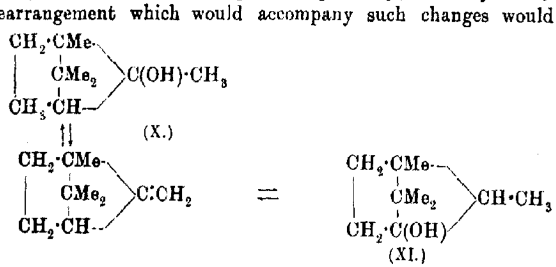
The relationship of all the derivatives of camphene, which have been mentioned above, to the present hydrocarbon and to each other can be stated very simply, as is shown in the scheme on p. 1905, on the assumption that camphene has the formula (III), which was originally proposed by Semmler, and which we consider to be the best expression of the known facts.

It must be noted that when camphene from *iso*borneol is oxidised with an alkaline solution of potassium permanganate, the chief product is the isomeride of camphoric acid, known as camphenecamphoric acid, and that some of this acid is also produced when nitric acid is used as the oxidising agent. It is known that camphenecamphoric acid is not an oxidation product of camphene glycol or of camphylic acid, but it has not yet been demonstrated that its constitution is different from that of camphoric acid. If it prove to be the case that these acids are differently constituted, and if at the same time it is assumed that camphenecamphoric acid has the same nucleus as camphene, the formation of this acid cannot be understood if either the formula given above (III) or Wagner's formula for camphene be adopted. The same difficulty arises in connexion with the acid, $C_{10}H_{16}O_2$, obtained by Henderson and Sutherland on oxidising camphene with hydrogen peroxide. There is no evidence, however, that the nuclei of camphene and of camphenecamphoric acid are identical. On the other hand, it is not at all improbable that camphene may undergo molecular rearrangement to some extent under the influence of such reagents as an alkaline



solution of potassium permanganate or hot nitric acid, and this appears to us a probable explanation.

The constitution of *iso*borneol is still uncertain, but it appears to be definitely proved that methylcamphenilol (X), the alcohol which is obtained from camphenilone by means of magnesium methyl iodide, is different from *iso*borneol. For the latter we suggest the formula below (XI), for if this is its constitution it is not difficult to understand the conversion of *iso*borneol into camphene, bornylene, borneol, or camphor respectively; at any rate, the rearrangement which would accompany such changes would be



much less profound than that which would be involved if camphene had the constitution represented by any of the other proposed formulæ.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CCXV.—*The Action of Chlorine on Alkalis and of Carbon Dioxide on Bleaching Powder.*

By ROBERT LLEWELLYN TAYLOR.

IN a former paper (Trans., 1910, **97**, 2541) I stated my conclusions that the action of chlorine on alkalis, like that of bromine and of iodine, is a reversible one, and that the action of carbon dioxide on bleaching powder and similar substances is like that of other acids, the carbonic acid decomposing both the hypochlorite and the chloride.

These conclusions are controverted by S. H. Higgins (this vol., p. 858), and it appears to be necessary to reply to some of his criticisms.

I had pointed out that if the action of chlorine on alkalis is a reversible one, the action would be reversed either (*a*) by the removal of free alkali, or (*b*) by the addition of chlorides to the solution. I showed by actually sweeping it out from the solution that free chlorine is developed in a solution of bleaching powder (*a*) by the removal of free lime, or (*b*) by the addition of chlorides; in the latter case, however, to only a slight extent unless some of the free lime is removed first. I further pointed out that the development of free chlorine naturally stimulates the bleaching action of the solution, and described experiments showing that the bleaching action of a solution of bleaching powder or of sodium hypochlorite is much more rapid after the removal of free alkali, or on the addition of common salt or calcium chloride, provided there is not too much free alkali present.

Higgins says (1) that it is not so much the removal of the free lime from the solution as the further action of the carbon dioxide of the air on the solution after the free lime has been removed that increases the bleaching efficiency; (2) that the action of common salt and of calcium chloride in increasing the bleaching efficiency is due "to the increased attraction of the carbon dioxide of the air by the salt solution"; (3) that other neutral salts of sodium have an effect similar to that of the chloride in stimulating the bleaching action when used in equivalent amounts.

With regard to (1) and (2) it is sufficient to point out that, in the great majority of the author's experiments, after the removal of free alkali or the addition of salt or calcium chloride to the solution, air had no access to the solution; or, when air was used, for example, for sweeping out the chlorine and hypochlorous acid in the solution, the carbon dioxide was removed from it first. Also, in the case of further experiments presently to be described, all of them were performed in closed vessels, to which air had no access. With regard to Higgins' statement (3) that "other neutral salts of sodium have an effect similar to that of the chloride in stimulating the bleaching action," it was considered desirable that further experiments should be made.

Sodium hypochlorite solution was prepared in three different ways: (1) by passing chlorine into a cold solution of sodium hydroxide, (2) by precipitating an aqueous solution of bleaching powder with a normal solution of sodium carbonate, so that the filtered liquid gave no precipitate with either of the solutions, and (3) by exposing a solution of bleaching powder to air in a shallow dish for a few hours, in order to remove some of the free lime, and then precipitating as in (2).

In preparing the hypochlorite by method (1), if the chlorine is passed in too long the solution smells of free chlorine, and bleaches very rapidly, and it is desirable to add more of the alkali. This was usually done until the odour of free chlorine had disappeared, and then the solution was diluted with water until it was of such a strength as to take a reasonable time for each experiment in bleaching.

The rate of bleaching was simply the time required, in comparative experiments, to more or less completely discharge the colour of similar small pieces of Turkey-red calico, previously wetted, and then immersed in the solutions.

The various solutions of hypochlorite were tried (*a*) alone, and (*b*) mixed with varying equivalent amounts of sodium chloride, sodium sulphate, and sodium nitrate. In some experiments the salts were weighed out and added in the solid state to the solutions, but more frequently measured quantities of standard solutions were used, containing respectively 117 grams of common salt, 322 grams of crystallised sodium sulphate, and 168 grams of sodium nitrate per litre.* In all such experiments the bleaching solution with which comparison was being made was diluted with water in volume equal to the amounts of the standard solutions used.

The results of a great number of experiments may be summarised as follows:

* These solutions are $2N$.

I.—If the solution of the hypochlorite contains a considerable excess of free alkali, its bleaching action is extremely slow. In some experiments, when the excess of free alkali was considerable, very little bleaching occurred, even after several days. In such solutions the rate of bleaching is almost unaffected by the addition of any of the salts above mentioned. When any appreciable effect does occur, there is very little difference in the effects of the different salts used. If anything, the sodium chloride has a rather greater effect than either the sulphate or the nitrate.

II.—With solutions of hypochlorite prepared by method (1) (see above), in which only just sufficient alkali was present to prevent the odour of free chlorine in the solution, many different experiments showed that sodium chloride accelerates the bleaching action very considerably, while sodium sulphate and sodium nitrate have little or no action. In some experiments, indeed, the sodium sulphate appeared to have a distinctly retarding effect on the bleaching. The following are two experiments out of many that were tried:

A. Five c.c. of the solution of sodium hypochlorite were used in each case. This was mixed with 5 c.c. of (*a*) water, (*b*) 2*N*-solution of sodium chloride, (*c*) 2*N*-solution of sodium sulphate, (*d*) 2*N*-solution of sodium nitrate. In (*b*) the Turkey-red calico was completely bleached in twenty-two minutes, whilst (*a*), (*c*), and (*d*) all took thirty-five minutes.

B. Same as above, but with a different solution of hypochlorite. In (*a*) the calico was bleached in thirty minutes, in (*b*) twenty minutes, in (*c*) forty minutes, and in (*d*) thirty minutes.

III.—Sodium hypochlorite prepared by method (2) (see above), seeing that solutions of bleaching powder are always strongly alkaline, naturally will also contain a considerable amount of free alkali. The solution therefore bleaches very slowly; but if it has been very carefully prepared, so that there is no excess of sodium carbonate, it practically behaves like the solution prepared by method I; its bleaching action is distinctly accelerated by the addition of sodium chloride, while sodium sulphate and nitrate have little or no effect. If, however, in preparing the solution, any considerable excess of sodium carbonate is used, this has almost the same effect as free alkali. The bleaching action is greatly retarded, and none of the sodium salts has any considerable effect in accelerating it.

IV.—The solution of sodium hypochlorite prepared by method (3) behaves in almost exactly the same way as that prepared by method (1); its bleaching action is greatly accelerated by sodium

chloride, and hardly at all by equivalent amounts of sodium sulphate and nitrate.

As already pointed out (p. 1907), all the above experiments were performed in closed vessels, so that air (other than the small amount which was already in the vessels) had no access; therefore the acceleration of the bleaching action could not have been due to carbon dioxide, as suggested by Higgins.

These additional experiments amply confirm my view as to the reversibility of the action of chlorine on alkalis.

The Action of Carbon Dioxide on Bleaching Powder.

Higgins (*loc. cit.*) also objects to my suggestion that the action of carbonic acid on bleaching powder is the same as that of other acids, the carbonic acid decomposing both the hypochlorite and the chloride. This view would be represented by the following equations:

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl.$

(2) $CaCl_2 + H_2O + CO_2 = CaCO_3 + 2HCl.$

(3) $2HOCl + 2HCl = 2H_2O + 2Cl_2.$

Instead of this, Higgins suggests that the action may be represented thus:

(1) $Ca(OCl)_2 + H_2O + CO_2 = CaCO_3 + 2HOCl.$

(2) $2HOCl + CaCl_2 + CO_2 = CaCO_3 + H_2O + 2Cl_2.$

On comparing these it is obvious that there is really very little difference between them. Higgins' equation (2) is simply a combination of my (2) and (3).

Higgins' equation (2) represents what is no doubt a complex action, and dividing it into two, as I suggest, simplifies it very considerably. As Higgins points out, the reaction is the reverse of Williamson's reaction for the effect of chlorine on water containing calcium carbonate in suspension:

$$CaCO_3 + 2Cl_2 + H_2O = 2HOCl + CaCl_2 + CO_2.$$

This also is a complex action, and doubtless takes place in two steps, the first being the action of chlorine on water (a reversible action), and the second the decomposition of calcium carbonate by hydrochloric acid:

(1) $2H_2O + 2Cl_2 \quad 2HOCl + 2HCl.$

(2) $CaCO_3 + 2HCl = CaCl_2 + H_2O + CO_2.$

I remember quite well that Williamson, in the 'sixties and 'seventies of last century, taught, in his lectures, that chlorine acts on water in the way represented above. He did not say in so many

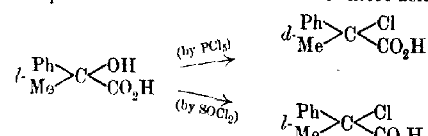
words that the action was a reversible one, but he probably had such a thing in his mind. He stated in his "Chemistry for Students," of which the last edition was published in 1873, that a solution of chlorine in water always contains both hypochlorous acid and hydrochloric acid, and that the presence of the latter was proved by the fact that silver chloride was precipitated from it when silver nitrate was added. There is hardly any doubt that Williamson would have offered the same explanation of the action of chlorine on water and calcium carbonate as the one suggested above.

MUNICIPAL SCHOOL OF TECHNOLOGY,
MANCHESTER.

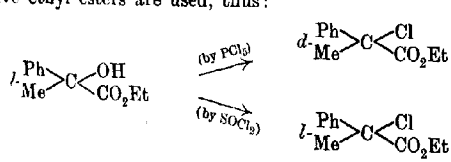
CCXVI.—*Experiments on the Walden Inversion. Part VII. Action of Phosphorus Pentachloride and of Thionyl Chloride on Optically Active Hydroxy-acids and Esters.*

By ALEX. MCKENZIE and FRED BARROW.

THE comparison of the behaviour of phosphorus pentachloride and of thionyl chloride towards the optically active α-hydroxy-α-phenylpropionic acids, which has been recently described by McKenzie and Clough (Trans., 1910, **97**, 2564), presents a novel aspect of the Walden inversion, inasmuch as, from the *l*-hydroxy-acid, for example, it is possible to obtain either a *d*- or *l*-chloro-acid, thus:



This is obviously an instance where either phosphorus pentachloride or thionyl chloride behaves abnormally, and it is interesting to note that the displacement of the hydroxy-group by the chlorine atom proceeds in a manner parallel with the above when the active ethyl esters are used, thus:



In the present paper an account is given of the action of phosphorus pentachloride and of thionyl chloride on a number of hydroxy-acids and esters. It is now established that a Walden inversion can be brought about in certain cases with esters of hydroxy-acids, and that the presence of a carboxyl group is not, therefore, a necessary condition for the occurrence of a Walden inversion.

The action of phosphorus pentachloride on *l*-mandelic acid is accompanied by much racemisation (McKenzie and Clough, Trans., 1908, **93**, 811), and the phenylchloroacetic acid formed possesses a dextrorotation which falls considerably below the maximum value. A change of sign of rotation also occurs, as Walden has shown (*Ber.*, 1895, **28**, 1287), when esters of *l*-mandelic acid are acted on by phosphorus pentachloride. The following changes have, accordingly, been already noted:

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \xrightarrow{\text{(by } PCl_5)} d\text{-}C_6H_5\cdot CHCl\cdot CO_2H,$$

and

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2Et \xrightarrow{\text{(by } PCl_5)} d\text{-}C_6H_5\cdot CHCl\cdot CO_2Et.$$

We now find that the action of thionyl chloride is different from that of phosphorus pentachloride, inasmuch as the following changes have been effected:

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \xrightarrow{\text{(by } SOCl_2)} l\text{-}C_6H_5\cdot CHCl\cdot CO_2H,$$

and

$$l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2Et \xrightarrow{\text{(by } SOCl_2)} l\text{-}C_6H_5\cdot CHCl\cdot CO_2Et.$$

Now, since it has been shown (Trans., 1908, **93**, 811) that *l*-phenylchloroacetic acid can be converted into *d*-mandelic acid by the action of water and silver carbonate, the interconversion of the active mandelic acids can be brought about according to the cycle:

$$\begin{array}{ccc} l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by } SOCl_2)} & l\text{-}C_6H_5\cdot CHCl\cdot CO_2H \\ \Big\uparrow \text{(by } Ag_2CO_3 \text{ and water)} & & \Big\downarrow \text{(by } Ag_2CO_3 \text{ and water)} \\ d\text{-}C_6H_5\cdot CHCl\cdot CO_2H & \xleftarrow[\text{(by } SOCl_2)]{} & d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \end{array}$$

which may be contrasted with the changes described previously, namely:

$$\begin{array}{ccc} l\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by } PCl_5)} & d\text{-}C_6H_5\cdot CHCl\cdot CO_2H \\ \Big\uparrow \text{(by NaOH)} & & \Big\downarrow \text{(by NaOH)} \\ l\text{-}C_6H_5\cdot CHCl\cdot CO_2H & \xleftarrow[\text{(by } PCl_5)]{} & d\text{-}C_6H_5\cdot CH(OH)\cdot CO_2H \end{array}$$

The racemisation which accompanies the displacement of the

hydroxy-group by the chlorine atom is much less pronounced when thionyl chloride is used in place of phosphorus pentachloride. In the case of the acid this is probably due to some extent to the fact that the action of thionyl chloride can be conducted at comparatively low temperatures. The phenylchloroacetic acid obtained by the interaction of thionyl chloride and *l*-mandelic acid had $[\alpha]_D$ $-101{\cdot}3°$ in benzene solution, whereas the pure acid, free from the *r*-isomeride, has $[\alpha]_D$ $-191°$ in the same solvent. Again the dextrorotatory ethyl phenylchloroacetate, prepared by Walden (*loc. cit.*) by the action of phosphorus pentachloride on a solution of ethyl *l*-mandelate in chloroform, had $[\alpha]_D$ $+25{\cdot}19°$, whilst the product obtained by the authors from thionyl chloride and ethyl *l*-mandelate possesses a much higher activity, namely, $[\alpha]_D$ $-64°$. A Walden inversion occurs, of course, in the case of the ester, either with phosphorus pentachloride or with thionyl chloride, but, although the racemisation is pronounced in the former case, this aspect can hardly be emphasised in favour of the view that phosphorus pentachloride acts abnormally.

The action of thionyl chloride on *r*-mandelic acid has been studied by Hans Meyer (*Monatsh.*, 1901, **22**, 415), who states: "Mandelsäure wird glatt unter Bildung von Benzaldehyd gespalten," and the formation of benzaldehyde is assumed to occur, owing to the disruption of the sulphito-chloride, $C_6H_5{\cdot}CH(OSOCl){\cdot}COCl$, with evolution of carbon monoxide and regeneration of thionyl chloride. We were unable to confirm this observation. Phenylchloroacetic acid is produced, although in small yield, by the action of water on the oil resulting from the treatment of *r*-mandelic acid with thionyl chloride, whilst the main product is benzylidene chloride. There was no evidence of the presence of benzaldehyde, and the action probably occurs according to the equations:

$$(1)\ C_6H_5{\cdot}CH(OH){\cdot}CO_2H + 2SOCl_2 = C_6H_5{\cdot}CH(O{\cdot}SOCl){\cdot}COCl + 2HCl + SO_2.$$

$$(2)\ C_6H_5{\cdot}CH(O{\cdot}SOCl){\cdot}COCl = C_6H_5{\cdot}CHCl_2 + SO_2 + CO.$$

$$(3)\ C_6H_5{\cdot}CH(O{\cdot}SOCl){\cdot}COCl = C_6H_5{\cdot}CHCl{\cdot}COCl + SO_2.$$

It is, however, conceivable that benzaldehyde is actually formed as an intermediate product, more especially since Hoering and Baum (*Ber.*, 1908, **41**, 1918) mention that benzylidene chloride can be formed in almost quantitative yield by the interaction of thionyl chloride and benzaldehyde.

As is well known, the action of phosphorus pentachloride on *l*-malic acid (or its esters) is accompanied by a change of sign of rotation (Walden). The authors have examined the behaviour of

thionyl chloride, and find that it is similar to that of pentachloride, thus:

$$l\text{-}\begin{matrix}CH(OH)\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix} \xrightarrow{\text{(by }SOCl_2)} d\text{-}\begin{matrix}CHCl\cdot CO_2H\\ CH_2\cdot CO_2H\end{matrix}$$

and

$$l\text{-}\begin{matrix}CH(OH)\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{matrix} \xrightarrow{\text{(by }SOCl_2)} d\text{-}\begin{matrix}CHCl\cdot CO_2Et\\ CH_2\cdot CO_2Et\end{matrix}.$$

The sulphito-ester, obtained from thionyl chloride and ethyl *d*-tartrate, was found to possess a much higher lævorotation than that quoted by Schiller (*Ber.*, 1909, **42**, 2017). Attempts to bring about the interconversion of the optically active tartaric acids by the aid of this compound were unsuccessful.

McKenzie and Wren (Trans., 1910, **97**, 1355) have already described the interconversion of the optically active α-hydroxy-β-phenylpropionic acids which has been effected according to the cycle:

$$\begin{array}{ccc} d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by }PCl_5)} & l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H \\ \Big\uparrow{\scriptstyle\text{(by }CaCO_3\text{ and water)}} & & \Big\downarrow{\scriptstyle\text{(by }CaCO_3\text{ and water)}} \\ d\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2H & \xleftarrow[\text{(by }PCl_5)]{} & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \end{array}$$

The oil obtained by the action of phosphorus pentachloride on the *d*-hydroxy-acid was dextrorotatory, but since it gave the *l*-hydroxy-acid on decomposition with calcium carbonate and water, it is probable that *d*-α-chloro-β-phenylpropionyl chloride corresponds in configuration with *l*-α-chloro-β-phenylpropionic acid. It was shown that the displacement of bromine in the active α-bromo-β-phenylpropionic acids gave hydroxy-acids of the same sign of activity as the bromo-acid used, no matter under what conditions the displacement was conducted; this action may be taken as normal. Further, it was pointed out that the action of phosphorus pentachloride is doubtless abnormal, the assumption being made that the behaviour of the active α-chloro-β-phenylpropionic acids towards calcium carbonate and water is similar to that of the α-bromo-β-phenylpropionic acids.

We have carried out a considerable number of experiments on the behaviour of the active ethyl esters of α-hydroxy-β-phenylpropionic acid towards phosphorus pentachloride and thionyl chloride respectively, and also on the action of thionyl chloride on the free acids. These changes are unfortunately complicated by the occurrence of side-reactions (compare Scheibler and Wheeler, *Ber.*, 1911, **44**, 2689), and our results have on this account little value. It is well known from the work of Anschütz and others that the action of phosphorus pentachloride on hydroxy-compounds

is frequently attended with the formation of phosphorus derivatives, whilst Bistrzycki and Landtwing (*Ber.*, 1908, **41**, 686), in continuation of the exhaustive researches of the former on carbon monoxide scission, have shown how readily the latter phenomenon occurs when certain acid chlorides are heated. It appears, however, that phosphorus pentachloride and thionyl chloride behave differently towards the active esters, inasmuch as the direction of rotation is unchanged with the former, and changed with the latter. The action of phosphorus pentachloride may accordingly be used to interconvert the acids as follows:

$$\begin{array}{ccc} l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by HCl and EtOH)}} & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2Et \\ & & \downarrow \text{(by } PCl_5) \\ d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xleftarrow[\text{(by } CaCO_3 \text{ and aqueous EtOH)}]{} & l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2Et \end{array}$$

Inasmuch as we find that the lævorotatory acid chloride resulting from the interaction of phosphorus pentachloride and the *l*-hydroxy-acid gives a lævorotatory ester when acted on by ethyl alcohol, it is possible that the acids can be interconverted according to the following changes:

$$l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H \longrightarrow l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot COCl \longrightarrow$$
$$l\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2Et \longrightarrow d\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H.$$

The contrast with thionyl chloride is indicated by the following scheme:

$$\begin{array}{ccc} l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2H & \xrightarrow{\text{(by HCl and EtOH)}} & l\text{-}C_6H_5\cdot CH_2\cdot CH(OH)\cdot CO_2Et. \\ & & \downarrow \text{(by } SOCl_2) \\ & \nwarrow \text{(by } CaCO_3 \text{ and aqueous EtOH)} & d\text{-}C_6H_5\cdot CH_2\cdot CHCl\cdot CO_2Et \end{array}$$

Since the bulk of the research on the Walden inversion has been confined to α-hydroxy-acids and their derivatives, the investigation of β-hydroxy-acids, where the carboxyl group is not directly attached to the asymmetric carbon atom, is of particular importance. At first it appeared that a Walden inversion could not be effected with this type, for example:

$$(1)\ l\text{-}CH_3\cdot CH(OH)\cdot CH_2\cdot CO_2H \underset{\text{(by } Ag_2O \text{ or water)}}{\overset{\text{(by } PCl_5)}{\rightleftarrows}} d\text{-}CH_3\cdot CHCl\cdot CH_2\cdot CO_2H$$

(E. Fischer and Scheibler, *Ber.*, 1909, **42**, 1219.)

$$(2)\ l\text{-}C_6H_5\cdot CH(OH)\cdot CH_2\cdot CO_2H \underset{\text{(by } Ag_2O \text{ or water or } Na_2CO_3)}{\overset{\text{(by HBr or } PBr_5)}{\rightleftarrows}} d\text{-}C_6H_5\cdot CHBr\cdot CH_2\cdot CO_2H$$

(McKenzie and Humphries, Trans., 1910, **97**, 121.)

(3) $d\text{-}C_6H_5{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H \xrightarrow{\text{(by } HNO_2)} l\text{-}C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$

$d\text{-}C_6H_5{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2Et \xrightarrow{\text{(by } HNO_2)} l\text{-}C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2Et$

(E. Fischer, Scheibler, and Groh, *Ber.*, 1910, **43**, 2020.)

It has, however, been recently shown by E. Fischer and Scheibler (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, **26**, 566; *Annalen*, 1911, **383**, 337) that the following changes can be carried out:

$$\begin{array}{ccc} d\text{-}CH_3{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H & \xrightarrow{\text{(by } HNO_2)} & l\text{-}CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \\ \downarrow{\scriptstyle\text{(by } NOCl)} & & \\ l\text{-}CH_3{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H & \xrightarrow{\text{(by water)}} & d\text{-}CH_3{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \end{array}$$

It is therefore obvious that a Walden inversion must have ccurred during one of these stages, and the phenomenon is accordngly not confined to α-substituted acids.

In this connexion we have studied the optically active β-hydroxy-β-phenylpropionic acids. The action of hydrochloric acid and of hosphorus pentachloride on the d-hydroxy-acid gives a lævorotatory hloro-acid, and when this is boiled with water the parent hydroxycid is regenerated (compare McKenzie and Humphries, *loc. cit.*), hus:

$$d\text{-}C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \underset{\text{(by water)}}{\overset{\text{(by } HCl \text{ or } PCl_5)}{\rightleftarrows}} l\text{-}C_6H_5{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H$$

The behaviour of thionyl chloride is, however, different, and the nterconversion of the hydroxy-acids was realised in accordance ith the following scheme:

$$\begin{array}{ccc} d\text{-}C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H & \xrightarrow{\text{(by } SOCl_2)} & d\text{-}C_6H_5{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H \\ \uparrow{\scriptstyle\text{(by water)}} & & \downarrow{\scriptstyle\text{(by water)}} \\ l\text{-}C_6H_5{\cdot}CHCl{\cdot}CH_2{\cdot}CO_2H & \xleftarrow[\text{(by } SOCl_2)]{} & l\text{-}C_6H_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H \end{array}$$

These changes are accompanied with a considerable amount of acemisation. It was noteworthy that the action of thionyl hloride gave a much more active acid chloride than in the case f phosphorus pentachloride; with thionyl chloride the crude roduct resulting from the d-hydroxy-acid had $\alpha_D^{17\cdot5} + 25{\cdot}38°$ in a 0 mm. tube, whilst with pentachloride α_D was only $-1{\cdot}25°$. The ormer product was necessarily contaminated with cinnamoyl hloride owing to the elimination of hydrogen chloride during the reparation; when, however, it was decomposed by water, the nnamic and the hydroxy-acid were easily separated from one nother. We consider it probable that the Walden inversion is aused by the thionyl chloride, and not by the water.

The above-mentioned cycle represents the first instance recorded of the interconversion of β-hydroxy-acids by the Walden inversion.

Experimental.

Action of Thionyl Chloride on r-*Mandelic Acid.*

Fifty grams of *r*-mandelic acid were heated with 100 grams of thionyl chloride for seven hours until the evolution of hydrogen chloride ceased. After removal of the excess of thionyl chloride, 30 grams of a pale yellow oil, boiling at 90—120°/13 mm., were collected, and then the product in the distilling flask began to decompose. Since the oil had not solidified when left overnight in contact with a large excess of water, it was separated from the latter by means of ether, and the acid present in the ethereal solution was removed by aqueous sodium carbonate. The phenylchloroacetic acid obtained from the sodium salt by acidification with mineral acid and extraction with ether amounted to 7·5 grams. The ethereal solution from which the phenylchloroacetic acid had been removed was evaporated, and the residual oil fractionated under diminished pressure, when it was found to consist mainly of benzylidene chloride. The latter compound was isolated without difficulty, and identified by its odour, boiling point, and analysis.

Action of Thionyl Chloride on l-*Mandelic Acid. Conversion of* l- *into* d-*Mandelic Acid.*

Ten grams of *l*-mandelic acid (1 mol.) and 24 grams of thionyl chloride (3 mols.) were heated at 50° for one hour, then boiled gently during two hours, and finally allowed to remain at the ordinary temperature for seven days. After removal of the thionyl chloride, the residual yellow oil was distilled under diminished pressure, when 4·5 grams, boiling at 97—102°/13 mm., were collected. This oil showed no tendency to solidify when left in contact with water overnight, whereas the product obtained by the interaction of phosphorus pentachloride and *l*-mandelic acid (Trans., 1908, **93**, 811) readily solidifies under these conditions. The phenylchloroacetic acid which was isolated as indicated in the preceding experiment amounted to 2·1 grams. It melted at 45—52° to a turbid liquid, which became clear at 65°, and was a mixture of the *r*- and *l*-acids, with the following rotation in benzene solution:

$$l=2,\ c=3\cdot656,\ \alpha_D^{16}\ -7\cdot41^\circ,\ [\alpha]_D^{16}\ -101\cdot3^\circ.$$

On crystallising this acid from a mixture of benzene and light petroleum, the crystals which separated contained a larger proportion of the racemic acid than did the original acid (compare Trans., 1909, **95**, 785), the following value for the specific rotation having been determined in benzene solution:

$$l=2,\ c=1\cdot702,\ \alpha_D^{14}\ -1\cdot49^\circ,\ [\alpha]_D^{14}\ -43\cdot8^\circ.$$

The mother liquor from this product was allowed to evaporate spontaneously at the ordinary temperature. The resulting phenylchloroacetic acid (1·05 grams) had, of course, a higher optical activity than that of the original acid. In benzene solution:

$$l = 2,\ c = 2{\cdot}394,\ \alpha_D^{14}\ -7{\cdot}00^\circ,\ [\alpha]_D^{14}\ -146{\cdot}2^\circ.$$

0·1265, dissolved in ethyl alcohol, required 23·5 c.c. $N/31{\cdot}5$-baryta for neutralisation, the calculated amount being 23·4 c.c.

The pure *l*-acid obtained by the resolution of the *r*-acid with morphine (*loc. cit.*) has $[\alpha]_D^{17}$ -191° in benzene solution.

When the chlorine in the above lævorotatory acid was displaced by the hydroxy-group by the aid of silver carbonate and water, a dextrorotatory mandelic acid was obtained. The chloro-acid (0·65 gram) with $[\alpha]_D$ $-146{\cdot}2^\circ$ was shaken with 40 c.c. of water at the ordinary temperature for half a minute, and then treated with silver carbonate, which had been freshly precipitated from 2 grams of nitrate. After one and a-half hours at the ordinary temperature with occasional shaking, the mixture was heated on the water-bath for one and a-half hours. Dilute hydrochloric acid was added, and the silver chloride removed. The filtrate (60 c.c.) was dextrorotatory, 25 c.c. of it in a 4-dcm. tube giving α_D $+1{\cdot}39^\circ$. The mandelic acid extracted from this solution in the usual manner gave the following value in ethyl-alcoholic solution:

$$l = 2,\ c = 1{\cdot}73,\ \alpha_D^{13}\ +1{\cdot}83^\circ,\ [\alpha]_D^{13}\ +52{\cdot}9^\circ.$$

Action of Thionyl Chloride on l-*Mandelic Esters.*

Methyl *l*-mandelate (4·3 grams) and thionyl chloride (12 grams) were mixed, and allowed to remain at the ordinary temperature for twenty-four hours. Since the action was incomplete, the solution was heated at 50—60° for one hour, and finally on the water-bath for two hours until the evolution of hydrogen chloride ceased. The ester was then distilled under diminished pressure, when 3·8 grams were obtained.

Methyl l-*phenylchloroacetate*, $C_6H_5{\cdot}CHCl{\cdot}CO_2Me$, is a colourless oil, boiling at 123—126°/11 mm.:

0·251 gave 0·1956 AgCl. Cl = 19·3.

$C_9H_9O_2Cl$ requires Cl = 19·2 per cent.

The specific rotation was determined:

$$l = 1,\ D_4^{15}\ 1{\cdot}213,\ \alpha_D^{15}\ -105{\cdot}15^\circ,\ [\alpha]_D^{15}\ -86{\cdot}7^\circ.$$

The hydrolysis of this ester was conducted as follows. One gram was added to 10 c.c. of aqueous hydrochloric acid saturated at 0°, and the mixture kept at the ordinary temperature for six days, with occasional shaking. When the viscid oil was nucleated with *l*-phenylchloroacetic acid, crystals began to form slowly after a time.

Water was added, and the mixture of acid and unattacked ester extracted with ether. The acid was removed from the ethereal solution by aqueous sodium carbonate, and was then isolated in the usual manner. The resulting phenylchloroacetic acid (0·42 gram) was lævorotatory in benzene solution:

$$l = 2,\ c = 2{\cdot}09,\ \alpha_D\ -3{\cdot}27^\circ,\ [\alpha]_D\ -78{\cdot}2^\circ.$$

0·1078, in ethyl-alcoholic solution, required 19·8 c.c. *N*/31·5-baryta for neutralisation. Calc., 19·9 c.c.

Ethyl *l*-mandelate (7 grams) and thionyl chloride (20 grams) were mixed, and kept at the ordinary temperature for four days, by which time the evolution of hydrogen chloride had ceased. ***Ethyl* l-*phenylchloroacetate*** is a colourless oil, and boils at 132—133°/15 mm.:

0·3366 gave 0·2406 AgCl. Cl = 17·7.

$C_{10}H_{11}O_2Cl$ requires Cl = 17·9 per cent.

The specific rotation was determined:

$$l = 0{\cdot}5,\ D_4^{16\cdot4}\ 1{\cdot}162,\ \alpha_D^{16\cdot4}\ -37{\cdot}18^\circ,\ [\alpha]_D^{16\cdot4}\ -64{\cdot}0^\circ.$$

The phenylchloroacetic acid obtained by conducting the hydrolysis in the manner already described in the case of the methyl ester was lævorotatory in benzene solution:

$$l = 2,\ c = 3{\cdot}26,\ \alpha_D\ -4{\cdot}38^\circ,\ [\alpha]_D\ -67{\cdot}2^\circ.$$

The displacement of chlorine in methyl *l*-phenylchloroacetate by alkyloxy-groups was examined. A solution of 1 gram of the chloro-ester in 10 c.c. of methyl alcohol was boiled for one and a-half hours with a solution of 0·4 gram of sodium in 5 c.c. of methyl alcohol. The sodium chloride was drained off, and the filtrate, when polarimetrically examined in a 2-dcm. tube, was found to be inactive. The acid isolated from the sodium salt was identified by its melting point and analysis as *r*-phenylmethoxyacetic acid.

The behaviour of sodium ethoxide towards the chloro-ester was similar.

This type of racemisation has a parallel in the observations of Purdie and Williamson (Trans., 1896, **69**, 820) dealing with the action of sodium ethoxide on ethyl *d*-α-chloropropionate and ethyl *l*-α-bromopropionate respectively. It was suggested by these authors that in actions of this type, halogen acid is eliminated with the subsequent addition of alcohol, a view which has support from the behaviour of esters of unsaturated acids towards alcohols in the presence of traces of sodium ethoxide.

Action of Thionyl Chloride on l-*Malic Acid.*

Eight grams of powdered *l*-malic acid and 28 grams of thionyl chlorides were allowed to remain at the ordinary temperature, when

low evolution of hydrogen chloride took place. After nine days solid present was removed, and found by analysis and ermination of rotation to consist of unaltered malic acid.

The displacement, however, of the alcoholic hydroxy-group in ic acid takes place readily under the following conditions. Six ms of the acid and 22 grams of thionyl chloride were heated the water-bath for one hour. The action was vigorous, and the gradually dissolved. The excess of thionyl chloride was oved under diminished pressure, and the residual viscid oil was olved in 50 c.c. of water. The chlorosuccinic acid was separated the malic acid present by extraction with ether. The yield rude chloro-acid was 2 grams, and, after one crystallisation from zene containing a little acetone, it melted at 174—176°. The cific rotation was determined in aqueous solution:

$$l = 2,\ c = 2.706,\ a_D^{18.5} + 1.09°,\ [a]_D^{18.5} + 20.1°.$$

Tilden and Marshall (Trans., 1895, **67**, 494) give $[a]_D^{13}$ −19.67° *l*-chlorosuccinic acid, obtained by the action of nitrosyl chloride *l*-asparagine. According to Walden (*Zeitsch. physikal. Chem.*, 5, **17**, 253), *d*-chlorosuccinic acid, obtained by the action of sphorus pentachloride on *l*-malic acid, melts at 174°, and has + 20.27°.

t is therefore possible to obtain readily by the above method pure *d*-chloro-acid by the action of thionyl chloride on *l*-malic d. Partial racemisation does, however, occur if the initial heating h thionyl chloride is prolonged. For example, when 7 grams *l*-malic acid were heated with 24 grams of thionyl chloride for e and a-half hours, the crude chlorosuccinic acid amounted to grams, and even after two crystallisations from benzene coning a little acetone, its melting point was low, namely, —159°, and its specific rotation in aqueous solution was only ·1°.

Action of Thionyl Chloride on Ethyl l-*Malate.*

Ethyl *l*-malate (7·6 grams, 1 mol.) was added to thionyl chloride 5 grams, 1 mol.), and, after four days at the ordinary temrature, the liquid was distilled under diminished pressure. The tical activity of the main fraction was determined, and the value tained did not alter when the product was redistilled. Yield, grams.

Ethyl d-*chlorosuccinate*, $CO_2Et{\cdot}CH_2{\cdot}CHCl{\cdot}CO_2Et$, is a colourless l, which boils at 124°/18 mm.:

0·2713 gave 0·1858 AgCl. Cl = 16·9.

$C_8H_{13}O_4Cl$ requires Cl = 17·0 per cent.

It has $D_4^{19.5}$ 1·152 and $a_D^{19.8}$ + 37·73° (l = 1); whence $[a]_D^{19.8}$ + 32·7°.

The latter value is higher than that quoted by Walden (*Ber.*, 1895, **28**, 1290), who prepared the ester from *d*-chlorosuccinic acid by the hydrogen chloride method, and obtained a product with $[\alpha]_D$ +27·5°. Walden's ester was thus partly racemised, but it is also doubtful if the compound, as obtained by us, possesses the maximum activity, especially since we find that partial racemisation does actually occur when the temperature is raised during the interaction of thionyl chloride (in slight excess) and ethyl *l*-malate. For example, 10 grams of the malate and 10 grams of thionyl chloride were allowed to remain for fifteen hours at the ordinary temperature, after which time a slight evolution of hydrogen chloride was still perceptible. The action was completed by boiling on the water-bath for three-quarters of an hour. The resulting ester had α_D^{18} +31·04° in a 1-dcm. tube. Further, the ester with $[\alpha]_D^{19\cdot 5}$ +32·7° gave a partly racemised chlorosuccinic acid when it was hydrolysed with fuming hydrochloric acid, but, of course, this effect may have been brought about during the hydrolysis; the chloro-acid obtained melted indefinitely at 162—166°, and had $[\alpha]_D$ +18·7° in aqueous solution.

Action of Thionyl Chloride on Ethyl d-*Tartrate.*

Carius (*Annalen*, 1859, **111**, 94) has shown that esters of sulphurous acid are formed by the interaction of thionyl chloride and alcohols, whilst Moers (*Inaug. Diss.*, Berlin, 1907) obtained the compound $(OEt)_2CH{\cdot}CH\Big<{}^{CH_2\cdot O}_{O\text{——}SO}$ by the action of thionyl chloride on glycerol acetal. Schiller (*Ber.*, 1909, **42**, 2017) accordingly studied the behaviour of tartaric esters towards thionyl chloride, and showed that the action proceeds thus:

$$\begin{matrix}CH(OH){\cdot}CO_2Et\\ |\\ CH(OH){\cdot}CO_2Et\end{matrix} + SOCl_2 = 2HCl + SO\Big<\begin{matrix}O{\cdot}CH{\cdot}CO_2Et\\ \quad |\\ O{\cdot}CH{\cdot}CO_2Et\end{matrix}.$$

Since this sulphito-ester, as described by Schiller, has a rotation opposite in sign to the tartrate used, we were led to prepare it with the object of regenerating tartaric acid from it in order to find out whether an interconversion of the active tartaric acids could be effected through a Walden inversion. Such an interconversion does not, however, occur.

The method employed differed in detail from that described by Schiller, and it gave a satisfactory yield of a product, which, on polarimetric examination, gave a value very much higher than Schiller's. Evolution of hydrogen chloride began at once at the ordinary temperature when 12 grams of thionyl chloride were added to 15 grams of ethyl *d*-tartrate. After two weeks at the ordinary

temperature, the thionyl chloride was removed, and the residue distilled under diminished pressure. A pale yellow oil was obtained boiling at 160°/12 mm., whereas Schiller gives 167°/11·5 mm. (Found, S = 12·6. Calc., S = 12·7 per cent.)

The following values were obtained:

$$l = 1,\ D_4^{19\cdot5}\ 1{\cdot}329,\ \alpha_D^{19\cdot5}\ -244{\cdot}3^\circ,\ [\alpha]_D^{19\cdot5}\ -183{\cdot}8^\circ;$$
$$l = 0{\cdot}5,\ D_4^{19\cdot5}\ 1{\cdot}342,\ \alpha_D^{19\cdot5}\ -124{\cdot}4^\circ,\ [\alpha]_D^{19\cdot5}\ -185{\cdot}4^\circ.$$

Schiller's values are as follows:

$$D^{19\cdot5}\ 1{\cdot}3257,\ [\alpha]_D^{17\cdot5-18}\ -56{\cdot}71^\circ.$$

We have also examined the compound in ethyl-alcoholic solution, with the result:

$$l = 2,\ c = 4{\cdot}703,\ \alpha_D\ -17{\cdot}78^\circ,\ [\alpha]_D\ -189{\cdot}0^\circ.$$

The ester was then decomposed by heating with aqueous sodium hydroxide, when sulphurous acid was readily eliminated. In this operation a change of sign of rotation occurred, and *d*-tartaric acid was obtained from the product by conversion into lead salt and decomposition of the latter with hydrogen sulphide.

Action of Phosphorus Pentachloride on d- *and* l-α-*Hydroxy-β-phenylpropionates.*

d-α-Hydroxy-β-phenylpropionic acid, prepared as previously described (Trans., 1910, **97**, 1355) by the resolution of the *r*-acid by morphine, was converted into its ethyl ester by the hydrogen chloride method.

Ethyl d-α-*hydroxy-β-phenylpropionate*,

$$C_6H_5{\cdot}CH_2{\cdot}CH(OH){\cdot}CO_2Et,$$

when freshly distilled, is a colourless oil, and boils at 152—154°/20 mm. It has D_4^{17} 1·105 and α_D^{17} +8·40°; whence α_D^{17} +7·6°.

On keeping overnight, the ester in the neck of the distilling flask used had solidified, and, after some days, a nucleus of this solid was added to the main lot of oil, when solidification of the latter occurred at once. Several preparations both of this ester and of its *l*-isomeride were carried out subsequently, but on no occasion did these esters fail to solidify soon after distillation, and when left exposed to the atmosphere of the laboratory, which had in the meantime doubtless become infected with the esters (compare Biilmann's work on the isomerism of the cinnamic acids).*

The solid *d*-ester melts at 46—47°:

0·2375 gave 0·5923 CO_2 and 0·1574 H_2O. C = 68·0; H = 7·4.

$C_{11}H_{14}O_3$ requires C = 68·0; H = 7·3 per cent.

* The corresponding *dl*-ester, prepared from ethyl β-phenyl-α-diazopropionate by Curtius and Müller (*Ber.*, 1904, **37**, 1268), is described as an oil.

The ester separates from light petroleum (b. p. 60—80°) in fine, long, felted needles. It is readily soluble in cold ethyl alcohol, benzene, or acetone, and, when its specific rotation was determined in these solvents, it was found to be lævorotatory in ethyl-alcoholic solution:

$$l=2,\ c=6\cdot074,\ \alpha_D^{18\cdot5}\ -0\cdot58°,\ [\alpha]_D^{18\cdot5}\ -4\cdot8°.$$

In benzene solution:

$$l=2,\ c=3\cdot982,\ \alpha_D^{17\cdot5}\ +1\cdot79°,\ [\alpha]_D^{17\cdot5}\ +22\cdot5°.$$

In acetone solution:

$$l=2,\ c=4\cdot272,\ \alpha_D^{17\cdot5}\ +1\cdot16°,\ [\alpha]_D^{17\cdot5}\ +13\ 6°.$$

The enantiomorphously related ester was also prepared from the *l*-acid.

Ethyl l-*α-hydroxy-β-phenylpropionate* boils at 159—160°/26 mm., and solidified on cooling. It has m. p. 46—47°, and the value for its rotation in benzene solution was in agreement with that of the *d*-ester:

$$l=2,\ c=4\cdot03,\ \alpha_D^{13}\ -1\cdot82°,\ [\alpha]_D^{13}\ -22\cdot6°.$$

The *l*-hydroxy-ester (6 grams) was heated with phosphorus pentachloride (6·7 grams) for about two hours at 100°, but, judging from the amount of pentachloride which had separated out overnight, it was obvious that the action was incomplete under these conditions. After one hour at 130°, the product was then distilled under diminished pressure, and the fraction boiling between 152° and 170°/18 mm. was collected. It was *lævorotatory*, giving $\alpha_D - 2\cdot2°$ in a 1-dcm. tube. Attempts to prepare a uniform product from it by further fractionation were unsuccessful. The various fractions, amounting to 5 grams, were then hydrolysed by boiling with calcium carbonate and aqueous alcohol, and a *dextrorotatory* aqueous solution of calcium salt was obtained, the observed value in a 2-dcm. tube being $\alpha_D + 0\cdot63°$.

The *d*-hydroxy-ester, when treated in chloroform solution with phosphorus pentachloride, gave a similar result.

The *l*-hydroxy-acid (4·7 grams) was acted on by phosphorus pentachloride (11·7 grams), as described by McKenzie and Wren (*loc. cit.*) for the *d*-acid. After distillation under diminished pressure, the product was lævorotatory, its solution in an equal volume of ether giving $\alpha_D - 8\cdot5°$ in a 1-dcm. tube. On treatment with ethyl alcohol, an oil was obtained; the main portion boiled at 162—171°/23 mm. The amount of material was too small to admit of further purification, but it was found that the liquid gave $[\alpha]_D - 12\cdot1°$ in ethyl-alcoholic solution.

Action of Thionyl Chloride on Ethyl l-*α-Hydroxy-β-phenylpropionate.*

Ethyl *l*-α-hydroxy-β-phenylpropionate (6 grams) and thionyl chloride (12 grams) were allowed to remain at the ordinary temperature for one and a-half hours, then heated within half an hour to 50°, and maintained at this temperature for one hour, and finally heated for two and a-half hours on the water-bath. On fractionation, 3·5 grams, b. p. 129—138°/8 mm., were obtained, and this was *dextrorotatory*, giving α_D +19·18° in a 50 mm. tube. On decomposition with calcium carbonate and aqueous alcohol, it gave an aqueous solution of calcium salt, which was *laevorotatory*.

Several experiments were also carried out on the action of thionyl chloride on the *r*- and *l*-hydroxy-acids with no positive result, owing to the decomposition which occurred during the distillation of the acid chloride.

Action of Hydrochloric Acid on d- *and* l-*β-Hydroxy-β-phenylpropionic Acids.*

The optically active acids were prepared from the *r*-acid by the method previously described (Trans., 1910, **97**, 121).

Eight grams of *d*-β-hydroxy-β-phenylpropionic acid were added to 120 c.c. of fuming hydrochloric acid (saturated at 0°), cooled to −10°. On shaking, the bulk of the hydroxy-acid dissolved, and, after ten minutes, the chloro-acid began to crystallise out. The mixture remained in the freezing mixture for two hours, and, after fifteen hours at the ordinary temperature, the voluminous precipitate was drained off; yield about 8 grams, $[\alpha]_D$ in ethyl-alcoholic solution −12°. The acid, when crystallised from benzene, separated in lustrous leaflets (6·2 grams) with $[\alpha]_D$ −7·1° in ethyl alcohol. This acid contained 18·85 per cent. Cl, whereas

$$C_6H_5 \cdot CHCl \cdot CH_2 \cdot CO_2H$$

requires 19·2 per cent. After one further crystallisation, the optical activity dropped to $[\alpha]_D$ −4·6° in ethyl alcohol. (Found, Cl = 19·0 per cent.) A change of sign of rotation took place when the chlorine in the latter acid was displaced by the hydroxy-group by boiling with water. A little cinnamic acid was formed in this operation. The resulting hydroxy-acid was slightly but distinctly dextrorotatory; a solution of 3 grams, made up to 20 c.c. of ethyl alcohol, gave α_D +0·29° in a 4-dcm. tube, and the dextrorotation still was evident when the product was crystallised from benzene.

The change

$$l\text{-}C_6H_5 \cdot CHCl \cdot CH_2 \cdot CO_2H \longrightarrow d\text{-}C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$$

was also confirmed by the action of water on the chloro-acid, obtained from the mother liquors, from which the acids with $[\alpha]_D$ $-7{\cdot}1°$ and $-4{\cdot}6°$ had been removed. Two grams of this acid with $[\alpha]_D$ $-21{\cdot}7°$ were boiled with water in an open flask for one and a-quarter hours. Some styrene was produced, and also a little cinnamic acid, which was removed. The hydroxy-acid was extracted with ether in a continuous extraction apparatus. It amounted to 1·1 grams, and was dextrorotatory, 0·8658, dissolved in ethyl alcohol and made up to 10 c.c., giving α_D $+0{\cdot}21°$ in a 2-dcm. tube. The dextrorotation persisted in the product obtained by crystallisation from benzene, the $[\alpha]_D$ being only $+0{\cdot}9°$ in ethyl alcohol. (Found, C=64·9; H=6·3. Calc., C=65·0; H=6·1 per cent.)

The optical activity of the crude chloro-acid varies considerably in value according to the conditions under which the action of hydrochloric acid is conducted. In the preceding experiment, the specific rotation of the crude acid was $-12°$, but in one experiment with the *l*-hydroxy-acid, when the product was removed after four hours at about $-15°$ in contact with fuming hydrochloric acid, the crude chloro-acid had $[\alpha]_D$ $+21{\cdot}8°$. On the other hand, in an experiment with the *l*-hydroxy-acid where the action was conducted at the ordinary temperature, the $[\alpha]_D$ of the product was only $+6{\cdot}5°$.

Action of Phosphorus Pentachloride on d-*β-Hydroxy-β-phenylpropionic Acid.*

Phosphorus pentachloride (21 grams) was gradually added to *d*-β-hydroxy-β-phenylpropionic acid (8 grams), the operation being conducted by cooling the mixture to $-15°$ from time to time in order to avoid, so far as possible, any racemisation which might occur by the temperature being too high. After five days at the ordinary temperature, a small amount of pentachloride remained unattacked, and the mixture was therefore heated for ten minutes until all dissolved. After removal of the phosphoryl chloride, the residue containing the chloro-chloride was *laevorotatory*, giving $\alpha_D^{17\cdot5}$ $-1{\cdot}25°$ in a 50 mm. tube. This oil was decomposed by moist ether, and the solid product containing the chloro-acid was also lævorotatory in ethyl-alcoholic solution:

$$l=4,\ c=8{\cdot}5184,\ \alpha_D\ -0{\cdot}44°,\ [\alpha]_D\ -1{\cdot}3°.$$

ction of Thionyl Chloride on d- *and* l-β-*Hydroxy*-β-*phenylpropionic Acids. Interconversion of the Acids.*

Preliminary experiments indicated that a sulphito-chloride is oduced by the action of thionyl chloride on the β-hydroxy-phenylpropionic acids, and that the change

$$C_6H_5\cdot CH(O\cdot SOCl)\cdot CH_2\cdot COCl \longrightarrow SO_2 + C_6H_5\cdot CHCl\cdot CH_2\cdot COCl$$

quires a fairly high temperature for its completion. The result- β-chloro-β-phenylpropionyl chloride also contained a large nount of cinnamoyl chloride due to the elimination of hydrogen loride.

A mixture of d-β-hydroxy-β-phenylpropionic acid (8 grams) and hionyl chloride (20 grams) remained at the ordinary temperature or fifteen hours, and was then boiled for twenty minutes. After emoval of the thionyl chloride, the residual oil was distilled under iminished pressure, when a large amount of gas was evolved. On e-distillation, a colourless, strongly refractive liquid (5 grams) was obtained, boiling at 137—137·5°/12 mm. It had $\alpha_D^{17.5}$ $+25{\cdot}38°$ in a 50 mm. tube, and a halogen determination showed that it contained no less than 48 per cent. of cinnamoyl chloride. It was hydrolysed by moist ether, and 3·8 grams of lustrous, colourless leaflets were obtained, which were examined in ethyl-alcoholic solution:

$$l = 2,\ c = 3{\cdot}836,\ \alpha_D^{16}\ +2{\cdot}54°,\ [\alpha]_D^{16}\ +33{\cdot}1°.$$

This product was separated into two fractions by crystallisation from benzene. The crystals which separated consisted of β-chloro-β-phenylpropionic acid and cinnamic acid, the latter being present to the extent of 39 per cent.; in ethyl-alcoholic solution, the value $[\alpha]_D$ $+21{\cdot}0°$ for $c = 4{\cdot}436$ was obtained. On evaporation of the mother liquor, the product gave $[\alpha]_D$ $+44{\cdot}7°$ for $c = 5{\cdot}498$.

The action of water on these mixtures of cinnamic acid, r- and d-β-chloro-β-phenylpropionic acids, was next investigated. The product (1·3 grams) with $[\alpha]_D$ $+21{\cdot}0°$ was boiled with water (50 c.c.) for several hours; the odour of styrene was perceptible, and, on cooling, cinnamic acid (0·62 gram) separated. The latter was removed, and the hydroxy-acid extracted with ether in a continuous apparatus. After crystallisation of the product from benzene, 0·42 gram of hydroxy-acid was obtained (Found, C = 64·9; H = 6·1. Calc., C = 65·0; H = 6·1 per cent.); it melted at 95—102°, and was a mixture of r- and l-β-hydroxy-β-phenylpropionic acids. The optical activity was slight, but distinct. In ethyl-alcoholic solution:

$$l = 0{\cdot}5,\ c = 13{\cdot}8,\ \alpha_D\ -0{\cdot}24°,\ [\alpha]_D\ -3{\cdot}5°.$$

The homogeneous *l*-acid, according to McKenzie and Humphries (*loc. cit.*), has $[\alpha]_D$ $-18{\cdot}9°$.

This result was confirmed by the action of water on the product with $[\alpha]_D$ $+44{\cdot}7°$. One and a-half grams of this, when decomposed by water, gave 0·55 gram of cinnamic acid and 0·55 gram of crude hydroxy-acid, which, after crystallisation from benzene, amounted to 0·44 gram. (Found, C = 65·0; H = 6·15. Calc., C = 65·0; H = 6·1 per cent.) In ethyl-alcoholic solution, the latter acid was lævorotatory:

$$l = 0{\cdot}5, \ c = 15{\cdot}33, \ \alpha_D \ -0{\cdot}44°, \ [\alpha]_D \ -5{\cdot}7°.$$

The residue remaining in the flask after distillation of the chlorochloride in the preceding experiment solidified on cooling, and was purified by crystallisation from ethyl alcohol, from which it separated in very pale yellow needles, melting at 134°. Yield, 1·1 grams. The compound proved to be optically inactive, and insoluble in sodium hydroxide. It had the properties of cinnamic anhydride, which, according to Liebermann, melts at 133°. (Found, C = 77·5; H = 5·3. Calc., C = 77·7; H = 5·1 per cent.) Its molecular weight in benzene solution gave the value 266 (calc., 278). Its phenylhydrazide separated from a mixture of ethyl alcohol and water in yellow needles, m. p. 186—187°, whereas Wedekind (*Ber.*, 1901, **34**, 2075) gives 187°.

The conversion of the *l*-hydroxy-acid into its *d*-isomeride was also carried out. The oil resulting from the action of thionyl chloride (28 grams) on *l*-β-hydroxy-β-phenylpropionic acid (10 grams) was distilled twice, and, as in the preceding experiment, a large quantity of gas was evolved during the first distillation. The product (6 grams) had α_D^{21} $-13{\cdot}75°$ in a 50 mm. tube, and boiled at 145—147°/23 mm. The mixture of chloro-acid and cinnamic acid obtained from it amounted to 5 grams, and had $[\alpha]_D$ $-14{\cdot}3°$ in ethyl-alcoholic solution. The hydroxy-acid, obtained from this by the action of water, was separated from cinnamic acid, and then gave $[\alpha]_D$ $+3{\cdot}4°$ in ethyl-alcoholic solution.

The authors are indebted to the Government Grant Committee of the Royal Society for a grant in aid of this research.

BIRKBECK COLLEGE,
LONDON.

CCXVII.—*The Relation between Residual Affinity and Chemical Constitution. Part II. Certain Compounds of Nitrogen.*

By Hans Thacher Clarke (1851 Exhibition Scholar).

In a previous communication (Trans., 1910, **97**, 416) an account was given of a study of the reactivity of the halogen atom in certain organic halogen compounds when allowed to react with alcoholic pyridine. In the present work an attempt has been made to examine the effects of chemical constitution in a series of simple aliphatic tertiary amines containing two nitrogen atoms by a study of their reactivity towards alcoholic benzyl chloride, under standard conditions, as well as by an examination of the refractive powers of the comparable members of this series. The results of the reaction-velocity measurements are more difficult to interpret than in the case of the halogen compounds; only those substances which are of similar constitution have therefore been directly compared, in order to avoid, so far as possible, the introduction of the indeterminable influence due to steric considerations, as well as those due to structure demonstrated by N. Menschutkin (*Ber.*, 1897, **30**, 2775, etc.).

In the course of an examination of the properties of diethoxythioxan,

$$\begin{array}{c} CH_2\cdot S\cdot CH_2 \\ EtO\cdot CH{-}O\cdot CH\cdot OEt \end{array}$$

Dr. Smiles and the present author (Trans., 1909, **95**, 992) were led to the conclusion that the sulphur and oxygen atoms situated in the 1:4-position in the saturated cyclic system exercised a mutual influence on each other, as shown by subnormal reactivity and exalted refractive power. In order to ascertain whether this phenomenon is constant throughout the series of six-membered cyclic compounds containing unsaturated atoms in the 1 : 4-positions, an extensive examination of such compounds has been undertaken. In the present paper the question of the piperazines is discussed.

The dialkylpiperazines may be prepared by the interaction of two molecules of ethylene bromide with two molecules of a primary amine, in the presence of some agent which will eliminate halogen hydride:

$$2R\cdot NH_2 + 2C_2H_4Br_2 + 4KOH = R\cdot N{<}\begin{array}{c}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{array}{>}N\cdot R + 4KBr + 2H_2O.$$

For purposes of comparison, the corresponding open-chain methyl derivatives of ethylenediamine were selected:

$$R\cdot N\begin{matrix}\diagup CH_2\cdot CH_2 \diagdown \\ \diagdown CH_3 \quad CH_3 \diagup\end{matrix}N\cdot R.$$

A comparison of the refractive powers of the two classes of compound is thus readily effected with a minimum possible error, merely by subtracting the atomic refractions of two hydrogen atoms from the dimethyl derivative.

In carrying out the reactivity measurements, equal volumes of an $N/2$-solution of benzyl chloride and an $N/4$-solution of the tertiary diamine (or an $N/2$-solution of the tertiary monoamine) in absolute alcohol were mixed and maintained at 56°, aliquot portions being withdrawn from time to time and titrated by Volhard's method with $N/25$-solutions of silver nitrate and potassium thiocyanate. Owing to the complicated nature of the reaction, velocity-constants were in general not obtainable; the results are therefore expressed graphically by plotting the percentage of quaternary ammonium salt formed against the time. For purposes of comparison, it may perhaps be convenient to quote the times necessary to bring about 10 per cent. of the complete reaction, assuming total combination to be in all cases possible.

The first series shows the relative reactivities of a simple tertiary amine, a tertiary diamine, and a disubstituted piperazine, these being selected so as to be as nearly as possible comparable:

		Time for 10 per cent. reaction.
Ethylpiperidine	$C_5H_{10}NEt$	40 mins.
Ethylenedipiperidine ...	$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot NC_5H_{10}$...	2 hrs., 45 mins.
Diethylpiperazine	$EtN\begin{matrix}\diagup CH_2\cdot CH_2 \diagdown \\ \diagdown CH_2\cdot CH_2 \diagup\end{matrix}NEt$	8 mins.

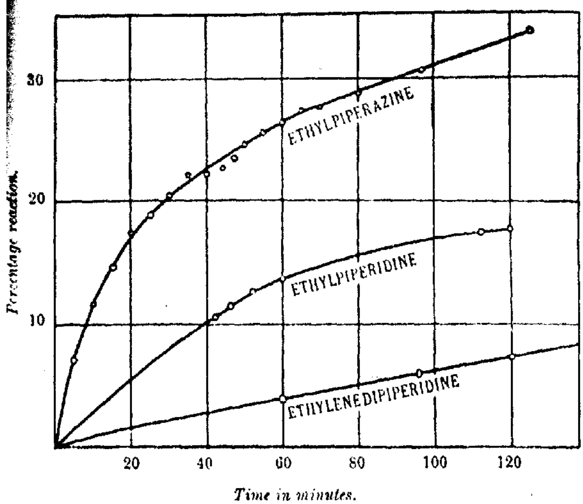
From this it is evident that ethylenedipiperidine, which may be regarded as a normal tertiary diamine, is far less reactive than diethylpiperazine, in which the unsaturated nitrogen atoms are situated in the 1:4-position in the ring. Ethylenedipiperidine is assumed to be normal, since the refractive power, 61·05 [as observed both by Brühl (*Zeitsch. physikal. Chem.*, 1895, **16**, 316) and the present author], agrees closely with the value calculated from the refractive power of methylpiperidine—31·58—as determined by Brühl (*loc. cit.*), and evaluated by the Lorentz-Lorenz formula:

	M_α (obs.).		M_α (calc.).	Δ.
Ethylenedipiperidine $C_5H_{10}N\cdot C_2H_4\cdot NC_5H_{10}$...........		$2C_5H_{10}NMe$......	63·16	
		Less 2H	2·18	
	61·05		60·98	+0·07

The values of the atomic refractions are taken from Eisenlohr's paper (*Zeitsch. physikal. Chem.*, 1910, **75**, 585).

Further examples of piperazine derivatives were compared with the corresponding open-chain compounds:

FIG. 1.



		Time for 10 per cent. reaction.
*iso*Amylpiperidine	$C_5H_{10}N\cdot C_5H_{11}$	1 hr., 40 mins.
Dimethyldi*iso*amylethylenediamine	$C_5H_{11}\cdot NMe\cdot C_2H_4\cdot NMe\cdot C_5H_{11}$	48 mins.
Di*iso*amylpiperazine	$C_5H_{11}N<^{C_2H_4}_{C_2H_4}>NC_5H_{11}$	37 mins.

		Time for 10 per cent. reaction.
Benzylpiperidine	$C_5H_{10}N\cdot CH_2Ph$	5 hrs., 10 mins.
Dibenzyldimethylethylenediamine	$CH_2Ph\cdot NMe\cdot C_2H_4\cdot NMe\cdot CH_2Ph$	17 hrs., 10 mins.
Dibenzylpiperazine	$CH_2Ph\cdot N<^{C_2H_4}_{C_2H_4}>N\cdot CH_2Ph$	12 hrs., 40 mins.

In both these cases the piperazine derivative is observed to be more reactive than a corresponding dimethyl derivative of ethylenediamine.

Refractive powers of these pairs of compounds were measured, and it was found that in each case the piperazine derivative

FIG. 2.

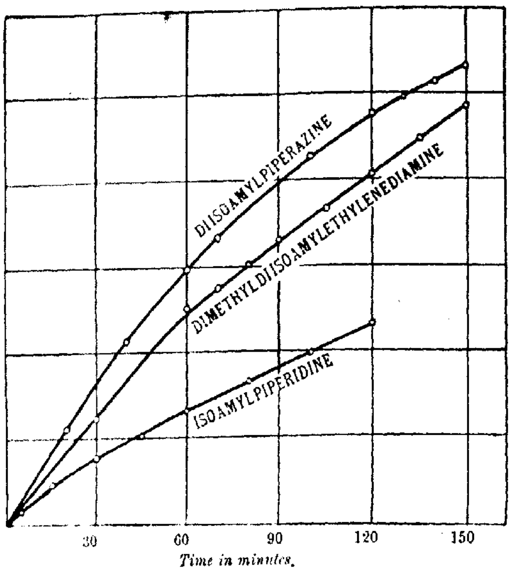
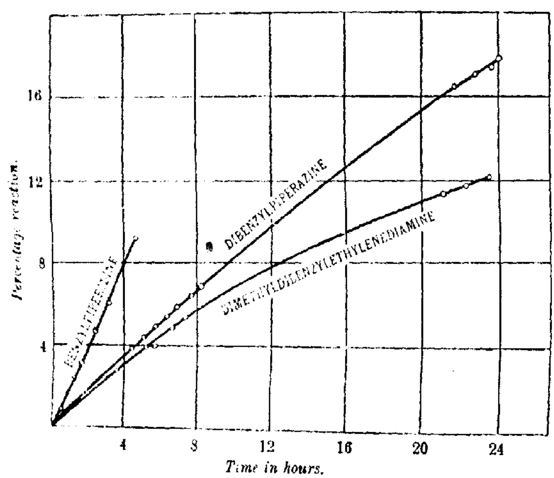

DIISOAMYLPIPERAZINE
DIMETHYLDIISOAMYLETHYLENEDIAMINE
ISOAMYLPIPERIDINE
Percentage reaction.
25
20
15
10
5
30
60
90
120
150
Time in minutes.

FIG. 3.


DIBENZYLPIPERAZINE
DIMETHYLDIBENZYLETHYLENEDIAMINE
Percentage reaction.
16
12
8
4
4
8
12
16
20
24
Time in hours.

exhibited a small but distinct exaltation, which is of the same order of magnitude as that observed for diethoxythioxan (+0·40).

	M_a (obs.).	M_a (calc.).	Δ.
Dimethyldi*iso*amylethylenediamine	74·12	—	—
Di*iso*amylpiperazine	72·46	71·94	+0·52
Dibenzyldimethylethylenediamine	85·52	—	—
Dibenzylpiperazine	83·83 (mean of three observations)	83·34	+0·49

Benzylpiperidine was also examined, and the value 55·65 observed for the molecular refractive power.

The calculation of the refractive power of the piperazines from that of the open-chain compound is effected in the ordinary manner.

	M_a.
Value for dimethyldi*iso*amylethylenediamine	74·12
Less value for two hydrogen atoms	2·18
Calculated value for di*iso*amylpiperazine	71·94
Observed ,, ,, ,,	72·46
Difference	+0·52

It may be noted that the value observed for benzylpiperidine (55·65) is normal, there being only a slight difference from the value calculated from those of methylpiperidine and toluene:

	M_a.
Methylpiperidine	31·58
Toluene	30·79
	60·37
Less CH_2+2H	6·78
Benzylpiperidine (calc.)	55·59
,, (obs.)	55·65
Difference	+0·06

The refractive powers of the corresponding phenyl open-chain and piperazine derivatives were determined, and the observed values compared with that of dimethylaniline (Brühl, *Zeitsch. physikal. Chem.*, 1895, **16**, 220):

	M_a (obs.).	M_a (calc.)	Δ.
Dimethylaniline, NMe_2Ph	40·38		
Diphenyldimethylethylenediamine, $NMePh·CH_2·CH_2·NMePh$	78·65 (mean of two observations)	78·58	+0·07
Diphenylpiperazine, $PhN<\begin{matrix}CH_2·CH_2\\CH_2·CH_2\end{matrix}>NPh$	77·52 (mean of two observations)	76·47	+1·05

Diphenyldimethylethylenediamine is optically normal when compared with dimethylaniline:

	M_a.
Twice value for dimethylaniline (40·38)	80·76
Less value for two hydrogen atoms	2·18
Calculated value for diphenyldimethylethylenediamine	78·58
Observed „ „	78·65
Difference	+0·07

The value for diphenylpiperazine is directly calculated from that observed for diphenyldimethylethylenediamine.

In all the above instances it will be observed that the piperazine compound exhibits a small but well-defined optical exaltation, while from the case of the phenyl derivatives it is evident that Brühl's rule—that ring-formation is without effect on refractive power—may break down when unsaturated atoms are situated in certain positions in the ring. Although the inferences from the reactivity measurements in the piperazine series as compared with the open-chain methyl compounds must be drawn with all reserve on account of indeterminable steric and other influences, it may doubtless legitimately be concluded from the above evidence that the nitrogen atoms in piperazine compounds exert a mutual influence with the effect of increasing their reactivity and exalting their refractive power.

An attempt has also been made to detect influences ascribable to "space conjugation." This phenomenon was first observed by Hilditch (Trans., 1909, **95**, 1578), who found that anomalous optical rotatory power occurred in active esters and salts of saturated aliphatic dicarboxylic acids in which the carboxyl groups were in the 1:5- and 1:6-positions in a normal chain.

The reactivity towards benzyl chloride of a series of derivatives of piperidine in which the nitrogen atoms were separated by one, two, and three methylene groups:

$$C_5H_{10}N\cdot[CH_2]_n\cdot NC_5H_{10},$$

was observed. Monomethylenedipiperidine was found to be highly reactive; ethylenedipiperidine fell to a far lower value, which was noticeably increased in the case of trimethylenedipiperidine:

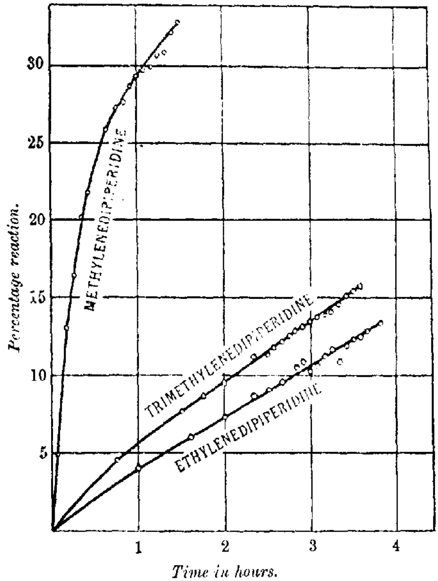
		Time for 10 per cent. reaction.
Methylenedipiperidine,	$C_5H_{10}N\cdot CH_2\cdot NC_5H_{10}$	7 mins.
Ethylenedipiperidine,	$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot NC_5H_{10}$	2 hrs., 46 mins.
Trimethylenedipiperidine,	$C_5H_{10}N\cdot CH_2\cdot CH_2\cdot CH_2\cdot NC_5H_{10}$	2 hrs., 8 mins.

Several attempts were made to prepare tetra- and penta-methylenedipiperidine, but without success. On condensing αε-dichloropentane with even a large excess of piperidine, the principal yield was

apparently the bicyclic quaternary ammonium chloride; only a very small quantity of an oil being obtained, which boiled above 300° under atmospheric pressure, and was insufficient for further purification. The quaternary chloride was not isolated.

From the above results it may be assumed that the two nitrogen atoms in methylenedipiperidine affect each other by virtue of their situation on the same carbon atom, in a manner similar to that of the halogen compounds described in a previous communication. Ethylenedipiperidine, in which the nitrogen atoms are situated

FIG. 4.



relatively in the 1:4-positions in the chain, may be regarded as normal. In trimethylenedipiperidine the nitrogen atoms are in the critical 1:5-position, and may be assumed to come into close proximity during their possible oscillations. This compound exhibits a reactivity above that of ethylenedipiperidine, so that it may without doubt justly be inferred that the spacial proximity induces the increased reactivity. The abnormality may be regarded as of the same type as that evinced by the piperazines, while the high reactivity of methylenedipiperidine may be attributed to a different cause.

The refractive powers of the derivatives of piperidine were measured, the following values being obtained:

	M_a.
Methylenedipiperidine	56·30
Ethylenedipiperidine	61·05
Trimethylenedipiperidine	65·62

Taking ethylenedipiperidine as the standard, and deducting or adding the refraction of the methylene group (4·60), methylenedipiperidine appears to be slightly depressed (−0·15), whilst trimethylenedipiperidine is almost exactly normal (−0·03). Refractive power therefore tends to throw no further light on the exalted reactivity of trimethylenedipiperidine. The author intends to enter more fully into the phenomena of space conjugation in a study of compounds of sulphur.

Experimental.

Methylenedipiperidine.—Prepared by Kraut's method (*Annalen*, 1890, **258**, 109) from piperidine and the condensation product of formaldehyde and sodium hydrogen sulphite. B. p. 235°. $D_4^{16·5}$ 0·9168, $n_a^{16·5}$ 1·47903; whence $M_a = 56·30$.

Ethylenedipiperidine.—From ethylene bromide and piperidine. B. p. 263°. $D_4^{16·5}$ 0·9236, $n_a^{16·5}$ 1·48720; whence $M_a = 61·05$.

Trimethylenedipiperidine.—From trimethylene bromide and piperidine. B. p. 278° [Tohl (*Ber.*, 1895, **28**, 2214) gives b. p. 274—275°]. D_4^{17} 0·9175, n_a^{17} 1·48520; whence $M_a = 65·62$.

s-*Dimethyldiisoamylethylenediamine.*—Four molecular proportions of methyl*iso*amylamine [prepared by Störmer and Lepel's method (*Ber.*, 1896, **29**, 2118) from *iso*valeraldehyde and methylamine, with subsequent reduction of the product] were treated in alcoholic solution under reflux with one molecular proportion of ethylene bromide in the presence of sodium acetate for four hours on the water-bath. After expelling the bulk of the alcohol and some unchanged methyl*iso*amylamine by distillation on the water-bath, the product was treated with aqueous alkali, extracted with ether, and the ethereal extract fractionally distilled under diminished pressure. The pure product was obtained in good yield as a colourless oil, boiling at 130—131°/18 mm., insoluble in water, miscible with organic liquids, which rapidly absorbs carbon dioxide from the atmosphere, with formation of a solid product:

0·0826 gave 0·2222 CO_2 and 0·1050 H_2O. C = 73·37; H = 14·19.

$C_{14}H_{32}N_2$ requires C = 73·68; H = 14·03 per cent.

$D_4^{19·2}$ 0·8083, $n_a^{19·2}$ 1·43855; whence $M_a = 74·12$.

Diisoamylpiperazine.—Equimolecular proportions of *iso*amylamine and ethylene bromide in alcoholic solution were warmed on the

water-bath under reflux for eight hours, with occasional addition of alcoholic potassium hydroxide in quantities just sufficient to remove ionisable bromine as a precipitate of potassium bromide. On completion of the reaction the mixture was filtered, the filtrate rendered faintly acid with hydrochloric acid, and the alcohol evaporated. The residue was dissolved in water, extracted with a small quantity of ether, then rendered strongly alkaline, and again extracted with ether. The ethereal solution, after being dried, was freed from ether, and the residue fractionally distilled under diminished pressure. The pure *diisoamylpiperazine* was obtained in poor yield as a colourless oil, boiling at 136—137°/18 mm., insoluble in water, miscible with organic liquids, and strongly basic:

0·1048 gave 0·2840 CO_2 and 0·1273 H_2O. C=73·91; H=13·49.

$C_{14}H_{30}N_2$ requires C=74·34; H=13·28 per cent.

D_4^{20} 0·83603, n_α^{20} 1·44860; whence M_α=72·46.

Benzylpiperidine.—From benzyl chloride and piperidine. B. p. 245°. D_4^{16} 0·9625, n_α^{16} 1·52420; whence M_α=55·65.

s-Dibenzyldimethylethylenediamine.—Four molecular proportions of benzylmethylamine were warmed for five hours on the water-bath under reflux with one molecular proportion of ethylene bromide in alcohol in presence of sodium acetate. The mixture was then filtered, the alcohol expelled on the water-bath, and the residue treated with concentrated aqueous sodium hydroxide and extracted with ether. The extract, after being dried, was freed from ether, and the residue distilled under diminished pressure. The fraction boiling above 195°/10 mm. was collected separately, and redistilled, when the pure product was obtained as a pale yellow oil, boiling at 198°/10 mm., insoluble in water, and miscible with organic liquids:

0·0981 gave 0·2902 CO_2 and 0·0804 H_2O. C=80·67; H=9·16.

$C_{18}H_{24}N_2$ requires C=80·59; H=8·95 per cent.

$D_4^{18·8}$ 0·9717, $n_\alpha^{18·8}$ 1·53244; whence M_α=85·52.

Dibenzylpiperazine.—Two samples were prepared; one from benzyl chloride and piperazine, and one from ethylene bromide and benzylamine in presence of alcoholic potassium hydroxide. In both cases the product was distilled under diminished pressure, and then recrystallised from alcohol. It melts at 92°.

I.—*In Alcohol.*

Solvent: $D^{18·6}$ 0·79982; $n^{18·6}$ 1·36138; wt. 3·3497.
Solution: D^{18} 0·81309; n^{18} 1·37235; wt. 3·5800.

M_α=83·88.

II.—*In Benzene.*

Solvent : D^{22} 0·87605 ; n^{22} 1·49484 ; wt. 1·9454.
Solution : D^{22} 0·89536 ; n^{22} 1·50360 ; wt. 2·2495.

$M_a = 83·72.$

III.—*In Benzene.*

Solvent : D^{22} 0·87605 ; n^{22} 1·49484 ; wt. 2·2425.
Solution : D^{22} 0·89215 ; n^{22} 1·50221 ; wt. 2·5225.

$M_a = 83·90.$

s-Diphenyldimethylethylenediamine.—Prepared by Dunlop and Jones' method (Trans., 1909, **95**, 418) from ethylene bromide and an excess of monomethylaniline at 100°. The product was distilled under diminished pressure, and then recrystallised from alcohol. It melted at 47·5°.

I.—*In Benzene.*

Solvent : D^{22} 0·87605 ; n^{22} 1·49484 ; wt. 3·1770.
Solution : D^{22} 0·89334 ; n^{22} 1·50536 ; wt. 3·5420.

$M_a = 78·54.$

II.—*In Benzene.*

Solvent : D^{22} 0·87605 ; n^{22} 1·49484 ; wt. 1·9015.
Solution : $D^{21·5}$ 0·89594 ; $n^{21·5}$ 1·50719 ; wt. 2·1476.

$M_a = 78·77.$

Diphenylpiperazine.—Prepared by the interaction of ethylene bromide and aniline in the presence of sodium carbonate. The product was distilled under diminished pressure, and recrystallised from alcohol. It melted at 163°.

I.—*In Benzene.*

Solvent : D^{22} 0·87605 ; n^{22} 1·49484 ; wt. 2·9416.
Solution : D^{21} 0·88517 ; n^{21} 1·50028 ; wt. 3·0895.

$M_a = 77·42.$

II.—*In Benzene.*

Solvent : D^{23} 0·87605 ; n^{22} 1·49484 ; wt. 3·6060.
Solution : D^{22} 0·88315 ; n^{22} 1·49915 ; wt. 3·7423.

$M_a = 77·63.$

Conclusions.

(1) The nitrogen atoms in *N*-substituted piperazines exert a mutual influence, occasioning optical exaltation.

(2) Tervalent nitrogen atoms in the "critical" positions in normal

chain compounds exert a similar mutual influence, but no optical anomaly has been detected in such substances.

(3) The reactivity towards organic halogen compounds of nitrogen atoms exerting such mutual influence is thereby increased.

The author desires to thank Dr. Smiles for valued advice and encouragement, and to express his gratitude to the Research Fund Committee of the Society for a grant in aid of the work.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CCXVIII.—*The Temperature-coefficient of the Electrical Conductivity of Hydrogen Chloride in Alcoholic Solution.*

By JAMES RIDDICK PARTINGTON.

IN a recent communication (Lapworth and Partington, this vol., p. 1417), the existing data for the conductivity of alcoholic hydrogen chloride were discussed, and it was remarked that the values of different observers were not in agreement. The conductivities at 25° were re-determined, and found to lie close to the values of Goldschmidt and Udby (*Zeitsch. Elektrochem.*, 1909, **15**, 5), except at high dilutions, when they were consistently lower than the latter. The value of λ_∞ at 25° was fixed at 66·5.

The number 43·10, recorded by Baly, Burke, and Marsden (Trans., 1909, **95**, 1100) as the result of experiments at 15° (of which no details are given), together with the temperature-coefficient of Völlmer (*Ann. Physik*, 1894, [iii], **52**, 328), leads to a value of λ_∞ at 25° which is certainly considerably lower than any other recorded value. It was therefore thought desirable to determine the conductivities at 0° and 18° (these temperatures being more conveniently maintained than 15°) with the purpose of finding whether, possibly, there might be some abnormality in the temperature-coefficient, and also of obtaining data on the electrical relations of hydrogen chloride which will be required in further investigations now in progress in this laboratory.

The apparatus consisted of cells of three different sizes, with platinised platinum electrodes, and closed with carefully ground glass stoppers. The constants were determined at 25° by means

of *N*/10-potassium chloride solution, the specific conductivity of which was taken as $k = 0{\cdot}01288$ mho.

Resistance measurements were made by means of a Nalder pattern Wheatstone bridge, with a small induction coil and telephone.

Alcoholic hydrogen chloride solutions were prepared and kept in the manner described in a previous communication (Trans., 1910, **99**, 1420).

The cells were cleaned with nitric acid and distilled water, and then carefully dried in an air-oven before each measurement. They were filled as rapidly as possible from a pipette, quickly stoppered, and the stopper covered with Faraday cement. The filling and closing of the cell must not occupy more than half a minute, otherwise the entrance of atmospheric moisture vitiates the results. The leads were joined through stout rubber tubing to glass tubes with mercury connexions, which were sealed into the sides of the cell, so that the whole could be sunk in a thermostat (compare Partington, this vol., p. 470), or immersed in clean, pounded ice, as required. The solutions could be kept for several days in carefully closed flasks in full daylight without altering in conductivity, but if allowed to remain for a day in the cell (that is, in contact with platinum), their conductivities decreased, and the solutions gave the Schiff reaction for aldehydes (compare Cohen, *Zeitsch. physikal. Chem.*, 1898, **25**, 1; Lapworth and Partington, this vol., pp. 1422, 1426). Measurements with solutions of very different concentrations, and extending over several hours, showed that steady values of the conductivity were reached after half an hour at 0°, and fifteen minutes at 18°; with very dilute solutions the conductivities changed appreciably after about twelve hours. The cells were frequently shaken during the measurements.

In the tables below are given (I) the concentrations in gram-molecules per litre, (II) the observed resistances in ohms, (III) the cell constants, (IV) the molecular conductivities, (V) the values of the latter from the smoothed curves. The values of λ_{∞} were obtained by the graphical method described in the previous communication. The values at the highest dilution were corrected for the conductivity of the specimen of alcohol used; for all other concentrations this correction was inappreciable.

Table I.

Conductivities at 0°.

(I.)	(II.)	(III.)	(IV.)	(V.)
0·850	39·5	0·42345	12·61	13·55
0·850	39·0	0·42345	12·77	
0·8446	39·58	0·40314	12·06	13·60
0·8446	39·24	0·40314	12·16	
0·585	47·70	0·40314	14·45	15·50
0·4086	58·92	0·40314	16·75	17·0
0·4086	58·80	0·40314	16·78	
0·2495	81·00	0·40314	19·95	19·95
0·115	158·00	0·42345	23·30	23·30
0·0853	40·15	0·08468	24·73	24·77
0·0853	40·00	0·08468	24·82	
0·0342	400·00	0·40314	28·86	
0·0342	399·6	0·40314	28·89	28·86
0·0342	400·3	0·40314	28·84	
0·023	578·1	0·40314	30·32	30·32
0·01079	338·8	0·12624	34·53	
0·01079	323·5	0·12624	36·17*	
0·01079	332·75	0·12624	35·16	34·45
0·01079	326·0	0·12624	35·89*	
0·01079	337·0	0·12624	34·72	
0·001079	2693·0	0·12624	42·64	
0·001079	2600·0	0·12624	42·35	40·35
0·001079	2685·0	0·12624	42·80	
0·001079	2720·0	0·12624	40·76	
0·00	151000·0	0·12624		

λ_∞ at 0° = 46·50 (extrapolated).

Table II.

Conductivities at 18°.

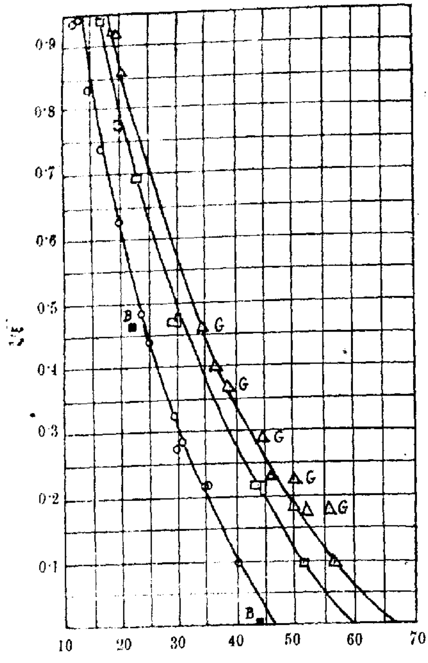
(I.)	(II.)	(III.)	(IV.)	(V.)
0·850	46·0	0·6472	16·55	16·45
0·850	46·6	0·6472	16·34	
0·4840	44·0	0·12624	19·83	20·50
0·3363	82·3	0·42345	23·38	23·38
0·1079	122·9	0·42345	31·93	31·50
0·1059	134·0	0·42345	29·73	31·55
0·1059	134·5	0·42345	29·73	
0·01059	270·0	0·12624	44·15	44·15
0·01059	270·0	0·12624	44·15	
0·001059	2190·0	0·12624	51·46	
0·001059	2190·0	0·12624	51·46	51·47
0·001059	2170·0	0·12624	51·96*	
0·001059	2150·0	0·12624	51·49	
0·00	1610000·0	0·12624	—	

λ_∞ at 18° = 60·00 (extrapolated).

(All values marked with asterisks were rejected in calculating the mean values.)

These results, along with those at 25° recorded in the previous paper, are represented graphically in Fig. 1, where λ is plotted against the cube root of the concentration. The values of

Goldschmidt and Udby (G) at 25°, and of Baly, Burke, and Marsden (B) at 15°, are added for comparison. The latter values are evidently much too small, and their position with respect to the curves makes it probable that they contain a large constant



○ *Conductivities at* 0°.
□ „ „ 18°.
Δ „ „ 25°.

error—possibly some arithmetical inaccuracy in connexion with the cell-constant. As these observers give no details, it is not possible to hazard any more definite explanation of the discrepancy.

The Temperature-coefficient of λ_∞.

If we assume that the molecular conductivity is a linear function of temperature:

$$\lambda = \lambda_0(1 + \alpha\theta),$$

where θ = temperature Centigrade, α = temperature-coefficient, we find, from the three values:

$$(a)\ \lambda_\infty = 46{\cdot}5 \text{ when } \theta = 0$$
$$(b)\ \lambda_\infty = 60{\cdot}0 \quad ,, \quad \theta = 18$$
$$(c)\ \lambda_\infty = 66{\cdot}5 \quad ,, \quad \theta = 25,$$

the following values of α_∞:

$$(a) \text{ and } (b)\ \alpha_\infty = 0{\cdot}0185$$
$$(a)\ \ ,,\ \ (c)\ \alpha_\infty = 0{\cdot}0172$$
$$\therefore \text{ Mean } \alpha_\infty = 0{\cdot}0178.$$

Summary.

The conductivities of alcoholic solutions of hydrogen chloride have been determined at 0° and 18°. The results of these experiments, together with those of previous experiments at 25°, have led to the following values for the limiting molecular conductivities and the temperature-coefficient α of the latter:

$$\lambda_\infty \text{ at } 0° = 46{\cdot}50$$
$$\lambda_\infty\ ,,\ 18° = 60{\cdot}00$$
$$\lambda_\infty\ ,,\ 25° = 66{\cdot}50$$
$$\alpha_\infty \text{ (mean)} = 0{\cdot}0178.$$

In conclusion, the author desires to thank Dr. A. Lapworth for the interest he has taken in the progress of the research.

SCHUNCK LABORATORY,
UNIVERSITY OF MANCHESTER.

CCXIX.—*The Absorption Spectra of the Nitration Products of Dimethyl*-p-*toluidine.*

By GILBERT T. MORGAN and ARTHUR CLAYTON.

IN continuance of their earlier investigations on the nitration of dimethyl-*p*-toluidine (Trans., 1905, **87**, 947; 1910, **97**, 2645), the authors have endeavoured to complete the series of nitro-derivatives of this tertiary base with the object of studying the effect of successive nitration on the colours and absorption spectra of these products.

Six of the nine theoretically possible nitro-derivatives of dimethyl-*p*-toluidine are known at present, together with several secondary nitration products (nitrosoamines and nitroamines), and an account

of the work is now put forward, inasmuch as the absorption spectra of polynitrated aromatic amines and their derivatives have not hitherto received much attention.

2:3:6-*Trinitrodimethyl*-p-*toluidine* (Formula VII).

A solution of one part of 2:6-dinitrodimethyl-*p*-toluidine in nine parts of concentrated sulphuric acid was diluted with fifteen parts of water, and the pasty mass thus produced treated with two to three parts of nitric acid (D 1·4), the mixture being heated at 95° for about ten minutes. The product, which was crystallised repeatedly from alcohol, separated in scarlet, flattened needles or plates, and melted at 137°:

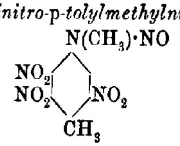
0·1116 gave 0·1652 CO_2 and 0·0399 H_2O. C=40·37; H=3·97.

0·1005 „ 18·4 c.c. N_2 at 22° and 760 mm. N=20·75.

$C_9H_{10}O_6N_4$ requires C=40·00; H=3·70; N=20·74 per cent.

The constitution of 2:3:6-*trinitrodimethyl*-p-*toluidine* is sufficiently indicated by the preparation of the base from 2:6-dinitrodimethyl-*p*-toluidine (Trans., 1910, **97**, 2645), as only one trinitro-derivative is theoretically possible.

2:3:6-*Trinitro*-p-*tolylmethylnitrosoamine*,



The action of highly concentrated nitric and sulphuric acids at high temperatures on the foregoing trinitro-base led to decomposition; milder treatment furnished the nitrosoamine with elimination of a methyl group from the tertiary amine radicle.

The pasty mass obtained by adding ten parts of water to the solution of one part of the trinitro-compound in nine parts of concentrated sulphuric acid was warmed for a short time at 80° with three parts of nitric acid (D 1·4), until the colour changed from red to yellow. The product was precipitated by ice-water, and crystallised from glacial acetic acid:

0·1403 gave 0·1751 CO_2 and 0·0366 H_2O. C=34·03; H=2·89.

0·0822 „ 17·3 c.c. N_2 at 19° and 766 mm. N=24·33.

$C_8H_7O_7N_5$ requires C=33·68; H=2·46; N=24·56 per cent.

2:3:6-*Trinitro*-p-*tolylmethylnitrosoamine* crystallises in yellow needles, melting at 162—163°, and giving the Liebermann reaction; it can also be prepared by heating the trinitro-base directly with a mixture of nitric acid (D 1·4) and 60 per cent. sulphuric acid.

2:5-*Dinitro*-p-*tolylmethylnitrosoamine* (Formula VIII).

A mixture of 2:5-dinitrodimethyl-*p*-toluidine (one part), 60 per cent. sulphuric acid (forty parts), and nitric acid (five parts, D 1·4) was heated for one hour at 100°, and the product crystallised from alcohol:

0·1672 gave 0·2460 CO_2 and 0·0596 H_2O. C=40·13; H=3·94.

0·1233 „ 25·0 c.c. N_2 at 18° and 760 mm. N=23·42.

$C_8H_8O_5N_4$ requires C=40·00; H=3·33; N=23·33 per cent.

2:5-*Dinitro*-p-*tolylmethylnitrosoamine* crystallises in pale yellow needles, melting at 126—127°; it is identical with one of the two nitrosoamines obtained by Pinnow from methyl-*p*-toluidine (*Ber.*, 1897, **30**, 840).

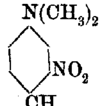
Action of Nitric Acid on 3:5-*Dinitrodimethyl*-p-*toluidine*.—This dinitro-base, when treated with mixtures of concentrated nitric and sulphuric acids at temperatures below 80°, remained unchanged; at higher temperatures a methyl group was eliminated, often with extreme violence owing to the formation of explosive methyl nitrate. The only definite products were 3:5-dinitro-*p*-tolylmethylnitrosoamine (m. p. 128°; Formula IX; compare Romburgh, *Ber.*, 1896, **29**, 1016) and the corresponding nitroamine. There was no indication of further nitration in the ring without elimination of a methyl group.

3:5-Dinitro-*p*-tolylmethylnitroamine (m. p. 138°; Formula X) was also prepared by the action of concentrated nitric acid (D 1·5) on the foregoing nitrosoamine (compare Gattermann, *Ber.*, 1885, **18**, 1482; Romburgh, *loc. cit.*; and Reverdin, *J. pr. Chem.*, 1911, [ii], **83**, 167).

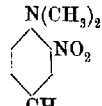
Absorption Spectra.

The absorption spectra of the nitrated dimethyl-*p*-toluidines and nitrated *p*-tolylmethylnitrosoamines were examined in absolute alcoholic solutions. The source of light was an iron arc, and a quartz spectrograph of high dispersive power was employed.

2-Nitrodimethyl-*p*-toluidine (m. p. 37°; Formula I; compare Trans., 1905, **87**, 947) was compared with its isomeride, 3-nitrodimethyl-*p*-toluidine (m. p. 25°; Formula II; Pinnow, *Ber.*, 1895, **28**, 3039), which was readily prepared in a solid form from its recrystallised sulphate. The absorption of the latter base has already been described by Baly, Tuck, and Marsden (Trans., 1910, **97**, 581):



(I.)



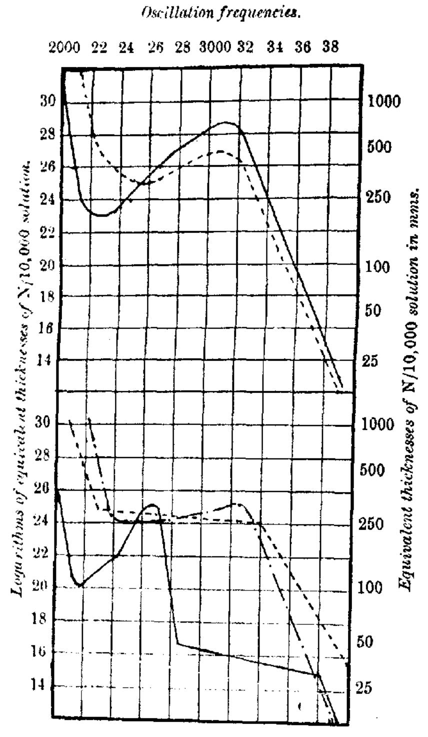
(II.)

The absorption curves of these two isomerides have the same general form, thus indicating similarity in constitution. The chief

FIG. 1.

Upper curves:

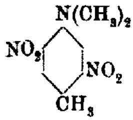
Full curve ——— 3-*Nitrodimethyl*-p-*toluidine.*
Dotted ,, - - - - - 2-*Nitrodimethyl*-p-*toluidine*



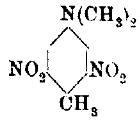
Lower curves:

Full curve ——— 2 : 5-*Dinitrodimethyl*-p-*toluidine.*
Dotted ,, - - - - - 3 : 5-*Dinitrodimethyl*-p-*toluidine.*
Dot and dash - — - 2 : 6-*Dinitrodimethyl*-p-*toluidine.*

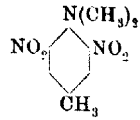
difference is that the absorption band of the ortho-nitroamine is nearer the red end (head of curve $1/\lambda$ 2290), and more persistent than the band ($1/\lambda$ 2560) of the meta-nitroamine:



(III.)



(IV.)



(V.)

2:5-Dinitrodimethyl-*p*-toluidine (Morgan and Clayton, *loc. cit.*), which contains its two nitro-groups unsymmetrically arranged with respect to the aminic radicle, shows an absorption band ($1/\lambda$ 2160) narrower than, but still comparable with, the bands exhibited by the two foregoing mononitro-bases. The remainder of the absorption curve (Fig. 1) departs from the form characteristic of aromatic mononitroamines in showing a very rapid change of absorption at certain dilutions, a step-out making its appearance at $1/\lambda$ 2820—$1/\lambda$ 3800.

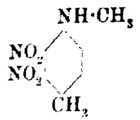
2:6-Dinitrodimethyl-*p*-toluidine (Morgan and Clayton, *loc. cit.*) gives a curve differing very considerably from those of the foregoing nitrated amines, and also from those of all other aromatic nitroamines which have been previously studied (compare Baly, Tuck, and Marsden, *loc. cit.*). The absorption band (head $1/\lambda$ 2550) is broadened and flattened almost to extinction, the remainder of the curve being comparable with that of 2-nitrodimethyl-*p*-toluidine.

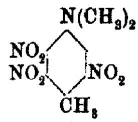
The 2:6-dinitro-base differs from the 2:5-dinitro-isomeride in containing its two nitro-groups symmetrically disposed with regard to the basic group, a fact which suggests that symmetry of the molecule may play an important part in diminishing the selective absorption exercised by the compound. This hypothesis is supported by the behaviour of 3:5-dinitrodimethyl-*p*-toluidine (m. p. 99—100°; Pinnow, *Ber.*, 1898, **31**, 2518). This base also contains its two nitro-groups in symmetrical positions with respect to the basic nitrogen, but in this instance they are both in ortho-, whereas in the former they are both in meta-positions. Since substituents in ortho-positions almost invariably affect each other more than when present in meta-positions, it is not surprising to find that the diminution of selective absorption attains its maximum in the case of 3:5-dinitrodimethyl-*p*-toluidine. The absorption band (Fig. 1) has disappeared, and is replaced by a step-out.

As it was not found possible to prepare 2:3-dinitrodimethyl-*p*-toluidine, the remaining isomeride of the above-mentioned bases, the corresponding 2:3-dinitromethyl-*p*-toluidine (Formula VI) was prepared and examined (Pinnow, *Ber.*, 1897, **30**, 833).

This comparison is quite justifiable, because Baly, Tuck, and Marsden (*loc. cit.*) have shown that in this group of nitro-compounds the mono- and di-methyl derivatives exhibit practically the same

absorption spectra, the only difference being that methylation shifts the absorption a little to the red:

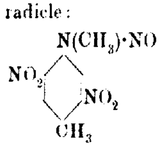

(VI.)

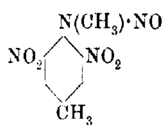

(VII.)

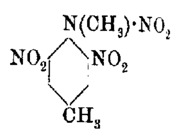
The substitution of a nitro-group in 2:6-dinitrodimethyl-*p*-toluidine to form 2:3:6-trinitrodimethyl-*p*-toluidine (VII) introduces into the molecule an element of dissymmetry which is manifested in the absorption curve (Fig. 2) by the reappearance of the band ($1/\lambda$ 2280), which, however, is comparatively shallow.

In 2:3-dinitromethyl-*p*-toluidine (VI), where the substituents are arranged consecutively, the maximum amount of dissymmetry is produced, and the absorption curve indicates a band ($1/\lambda$ 2280) which is the most persistent of any exhibited by this series of nitrated amines.

An examination of the absorption spectra of 2:5-dinitro- and 3:5-dinitro-*p*-tolylmethylnitrosoamines shows, however, that this effect of dissymmetry is exhibited only when the basic aminic group is present in the molecule. This basicity is considerably diminished by the replacement of one methyl group by a nitroso- or nitro-radicle:


(VIII.)


(IX.)


(X.)

The absorption curves of 2:5-dinitro-*p*-tolylmethylnitrosoamine (VIII) and 3:5-dinitro-*p*-tolylmethylnitrosoamine (IX) indicate a very similar general absorption (Fig. 2), although the former compound contains its nitro-groups unsymmetrically arranged with regard to the aminic nitrogen, whilst the nitro-groups of the latter isomeride are disposed symmetrically in this respect.

3:5-Dinitro-*p*-tolylmethylnitroamine (X) when first discovered was regarded as a trinitromethyl-*p*-toluidine (Gattermann, *loc. cit.*), but its absorption curve is quite comparable with those of the foregoing nitrosoamines, thus furnishing spectroscopic evidence in support of Romburgh's observation that one of the three nitro-groups is attached to nitrogen (*Rec. trav. chim.*, 1882, **3**, 404).

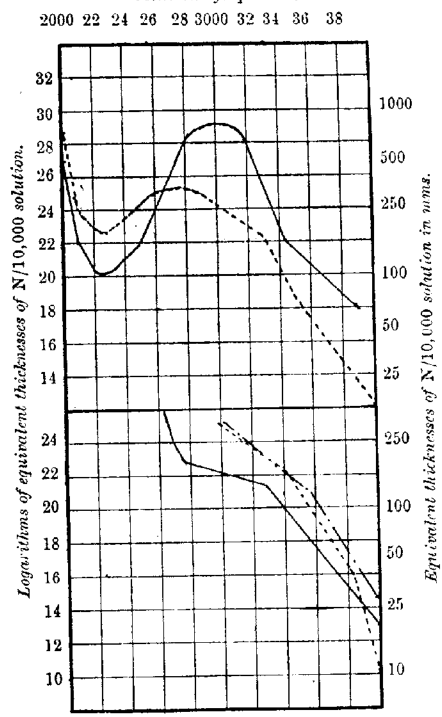
The Colour of Aromatic Nitroamines.

The introduction of an amino-group into the benzene nucleus nvolves a complete change in the absorption spectrum of this

FIG. 2.

Upper curves:

Full curve ——— 3 : 5-*Dinitromonomethyl*-p-*toluidine.*
Dotted ,, - - - - - 2 : 3 : 6-*Trinitrodimethyl*-p-*toluidine.*



Lower curves:

Full curve ——— 2 : 5-*Dinitro*-p-*tolylmethylnitrosoamine.*
Dotted ,, - - - - - 3 : 5-*Dinitro*-p-*tolylmethylnitrosoamine.*
Dot and dash - — - 3 : 5-*Dinitro*-p-*tolylmethylnitroamine.*

hydrocarbon. The seven small bands of benzene disappear, and the new spectrum exhibits one broad, well-defined band in the ultra-violet (Baly and Collie, Trans., 1905, **87**, 1343). The conversion

of colourless aniline into the yellow nitroanilines is not accompanied by any such marked alteration in the general character of the absorption, the change consisting mainly in a shift of the absorption band into the visible region of the spectrum, and in a persistence of the absorption at greater dilutions.

The question of relationship between the colour and constitution of benzenoid nitroamines is accordingly a special case of the general problem of the connexion between the selective absorption of aromatic bases and their chemical configuration.

It is customary to regard the nitro-group as the chromophor in nitroamines, but this effect is not specific, for other complexes play a similar part. In the aminocoumarins and their alkyl derivatives the unsaturated lactonic ring is the chromophor (Trans., 1904, **85**, 1230; 1910, **87**, 1350), and β-anthramine and di-*o*-aminostilbene exhibit colour in the absence of any substituent (*Annalen*, 1882, **212**, 57; *Ber.*, 1895, **28**, 1411).

The hypothesis that the colour of nitroanilines is due to a quinoid rearrangement of the molecule involving migration of hydrogen to the nitro-group, has been refuted by Baly, Tuck, and Marsden (*loc. cit.*), who showed that 3-nitro-*p*-toluidine and its methyl and dimethyl derivatives give absorption curves which are almost superposable, excepting that methylation shifts the band towards the red. Similar relationships were observed with the nitroanilines and their dialkyl derivatives.

With one nitro-group in the ring, variation in the orientation does not greatly modify the spectrum, but in general the band of the ortho- and para-derivatives is more persistent than that of the meta-isomeride.

As shown in the present communication, the effect produced by a second nitro-group depends largely on its position in relation to the aminic radicle and to the nitro-group already present. The question arises whether the exceptional form of the absorption curves of 2:6- and 3:5-dinitrodimethyl-*p*-toluidine is due to some alteration in the configuration of the aromatic nucleus consequent on the symmetrical grouping of the two nitro-groups about the basic radicle.

Kaufmann has suggested (*Ber.*, 1902, **35**, 3668) that nitro- and amino-derivatives of benzene contain respectively the aromatic nucleus in centric and para-quinonoid conditions, the latter corresponding with Dewar's benzene formula. In accordance with this view, one might expect that increase in the number of nitro-groups would result in a change from the spectrum of the nitroanilines to that exhibited by nitrobenzene. But the absorption curve of

2 : 3 : 6-trinitrodimethyl-*p*-toluidine is nearer to the characteristic nitroamino-form than that of 2 : 6-dinitrodimethyl-*p*-toluidine.

Moreover, Hantzsch has compared the spectrum of 3 : 5-dinitroaniline with that of 5-nitro-1 : 3-phenylenediamine, a base having an equally symmetric molecule, but a preponderance of amino-groups. The two curves are very similar, the bands occurring nearly in the same region of the spectrum, but, on the other hand, these absorption spectra are entirely different from that of 1 : 3 : 5-trinitrobenzene, which has no absorption band (*Ber.*, 1910, **43**, 1669).

It seems reasonable to infer that, in so far as mono-, di-, and tri-nitroamines are concerned, any change in the aromatic nucleus which may result from successive nitration is not such as can be indicated by differences in structural formulæ (compare Hartley, Trans., 1885, **47**, 693). This conclusion has also been reached by Hantzsch (*loc. cit.*), who regards the nitroanilines and their alkyl derivatives as having the conventional formula, but with the nitro-groups linked by subsidiary valencies to the hydrogen or alkyl radicles of the amino-group.

The fact that the character of the absorption is altered completely by the saturation of the aminic group suggests, however, that the predominant factor is the residual affinity of basic nitrogen. The shift of the absorption into the visible region of the spectrum may be regarded as due to a chemical change of the nature of internal salt formation, since it is independent of the relative positions of the amino- and nitro-groups involved. When the residual affinity of the basic nitrogen is directed wholly towards one nitro-group or towards two contiguous nitro-groups, then the molecule becomes unevenly strained, and a well-defined absorption band is manifested. If, however, this residual affinity is divided between two similarly situated nitro-groups, then the atomic stresses may be supposed to be more evenly distributed in the molecule, with the result that less selective absorption takes place.

The authors desire to express their thanks to Dr. W. B. Tuck for his kind assistance in preparing the photographs and absorption curves, and to the Research Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

THE ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CCXX.—*Decomposition of Hydrazides and Hydrazones by Heat.*

By Frederick Daniel Chattaway, Charles Linaeus Cumming, and Bernard Howell Wilsdon.

In continuation of an investigation of the behaviour of hydrazines at a high temperature, the reactions which take place when various hydrazides and hydrazones are heated have been studied.

When a phthalylhydrazide is heated, vigorous action accompanied by the evolution of heat sets in at a definite temperature, nitrogen and ammonia are liberated, and a phthalanil is produced, thus:

$$3C_6H_4{<}{}^{CO}_{CO}{>}N{\cdot}NHR = 3C_6H_4{<}{}^{CO}_{CO}{>}NR + N_2 + NH_3.$$

When a hydrazone is heated, two main reactions take place, resulting in the formation of an unsaturated hydrocarbon, nitrogen, and a saturated hydrocarbon, thus:

$$2CHR{:}N{\cdot}NHR' = CHR{:}CHR + 2N_2 + 2R'H,$$

and in the formation of an alkylideneaniline, nitrogen, and ammonia, thus:

$$3CHR{:}N{\cdot}NHR = 3CRH{:}NR' + N_2 + NH_3.$$

The two reactions proceed simultaneously, a somewhat larger amount of the hydrazone as a rule undergoing the latter decomposition.

Experimental.

Decomposition of Phthalylphenylhydrazide by Heat.

Phthalylphenylhydrazide when crystallised from alcohol, which is the most convenient solvent to employ, is usually obtained as a mixture of two polymorphic modifications; the crystals of one are bright yellow, those of the other almost colourless. The yellow form is the one stable at temperatures near its melting point (180°), the colourless variety being transformed into the yellow form without melting before this temperature is reached.

One hundred grams of phthalylphenylhydrazide were melted, and heated slowly in an oil-bath. When the fused mass reached a temperature of about 346°, a vigorous reaction set in, accompanied by the evolution of heat and liberation of nitrogen and ammonia. This temperature was maintained until all action had ceased, when the viscid liquid remaining was distilled. The bulk of it passed over as an orange-yellow liquid, which solidified on cooling to a resin-like solid, a small quantity of coked residue being

eft in the distilling flask. The solid distillate was recrystallised from alcohol and glacial acetic acid, and separated in fine, very pale yellow-coloured needles, melting at 208°.

From the mother liquors a small quantity of phthalimide was isolated.

The pale yellow, crystalline product, which formed practically the whole of the distillate, proved to be almost pure phthalanil, the colour being due to a very minute quantity of some yellow-coloured compound, probably a little of the original hydrazide which had escaped decomposition; this could be removed by boiling an alcoholic solution for a long time with animal charcoal, and repeated recrystallisation. A quantity carefully purified in this way melted sharply at 210°, and was identical in every respect with phthalanil made from phthalic anhydride and aniline, which also, when pure, melts at 210°. (Found, C=75·22; H=4·07; N=6·34; M.W.*=222·7. Calc., C=75·31; H=4·06; N=6·28 per cent. M.W.=223.)

The amounts of nitrogen and ammonia liberated were estimated by carrying out the decomposition of known quantities of the hydrazide in a current of carbon dioxide and hydrogen respectively; but owing to the time required to complete the decomposition, exact quantitative yields could not be obtained. The results, however, show conclusively that phthalylphenylhydrazide when heated decomposes thus:

$$3C_6H_4<\substack{CO\\CO}>N\cdot NHPh = 3C_6H_4<\substack{CO\\CO}>NPh + N_2 + NH_3.$$

*Decomposition of Phthalyl-*p*-bromophenylhydrazide by Heat.*

A similar reaction to that described above occurs when phthalyl-*p*-bromophenylhydrazide is heated, but owing to auto-reduction which goes on simultaneously, considerable quantities of hydrogen bromide are evolved. On distilling the solid product of the decomposition and recrystallising the distillate from alcohol, *p*-bromophthalanil was obtained, crystallising in fine needles (m. p. 204°), and identical with the compound obtained from phthalic anhydride and *p*-bromoaniline.

Decomposition of the Phthalyltolylhydrazides by Heat.

Only the deep yellow-coloured modifications of phthalyl-*o*- and -*p*-tolylhydrazide have up to the present been prepared, the exact conditions necessary for the deposition of the colourless modifications from solution not having yet been realised.

Phthalyl-*p*-tolylhydrazide behaves on heating exactly as does

* By determining the elevation of the boiling point of acetone.

phthalylphenylhydrazide. Twenty grams were similarly heated when at about 360° a vigorous reaction set in; heat as before was evolved, whilst nitrogen and ammonia were liberated. The yellow residue obtained when the action had completed itself was recrystallised from alcohol, and *p*-tolylphthalimide was obtained, crystallising in fine needles (m. p. 204°), and identical in every respect with the compound prepared by the interaction of phthalic anhydride and *p*-toluidine. Phthalyl-*o*-tolylhydrazide when heated behaved similarly, nitrogen and ammonia were given off, and *o*-tolylphthalimide could be isolated from the residue, but other subsidiary reactions which have not yet been investigated appeared to take place to a much greater extent than in the case of the para-compound.

Decomposition of Benzaldehydephenylhydrazone by Heat.

Benzaldehydephenylhydrazone (m. p. 156°) was placed in a small flask attached to a series of condensers, and gradually heated in an oil-bath. It commenced to decompose at about 210°, and at a temperature a few degrees higher a vigorous action took place, ammonia, nitrogen, and a liquid smelling strongly of benzene being produced. The liquid residue in the flask was heated until gas was no longer given off. The amounts of nitrogen and ammonia produced from weighed quantities of the hydrazone were determined by carrying out the decompositions in a current of carbon dioxide or of hydrogen. The liquid distillate was fractionated, and found to consist of benzene mixed with a very little toluene. The residue after all gas evolution had ceased was fractionally distilled in a vacuum. The lower fractions on cooling solidified to a white, crystalline mass, which on recrystallising from alcohol proved to be stilbene. It crystallised in white, glistening plates, which melted at 124°, and had the peculiar characteristic odour of the hydrocarbon. To complete the identification it was converted into the dibromide, which melted at 237°.

The fractions of higher boiling point which only slowly solidified proved to be benzylideneaniline, $C_6H_5 \cdot CH:N \cdot C_6H_5$.

Benzaldehydephenylhydrazone, therefore, when heated decomposes in two different ways. In one decomposition, stilbene, nitrogen, and benzene are produced, thus:

$$2CHPh:N \cdot NHPh = CHPh:CHPh + 2N_2 + 2C_6H_6,$$

a reaction recalling the behaviour of benzylideneazine when heated.

In the other, benzylideneaniline, nitrogen, and ammonia are formed, thus:

$$3CHPh:N \cdot NHPh = 3CHPh:NPh + N_2 + NH_3,$$

a reaction similar to that which the phthalylhydrazides undergo

when heated. The greater part of the benzaldehydephenylhydrazone decomposes in the latter manner.

The small amount of toluene found is, without doubt, formed by the reduction of the benzylidene group by the hydrazine group, a little diphenyl, which could not be recognised in presence of the stilbene, being possibly also produced.

Decomposition of Benzaldehydetolylhydrazones by Heat.

Benzaldehyde-*p*-tolylhydrazone melts at 120° to a red liquid, which at about 190° decomposes, with evolution of heat, nitrogen, ammonia, and a small amount of toluene being liberated. After the evolution of gas has ceased, if the residual liquid is distilled, a yellow, viscid, oily substance passes over, which on cooling deposits crystals of stilbene. The oily liquid which can be filtered from them is benzylidene-*p*-toluidine, and yields benzaldehyde and *p*-toluidine when hydrolysed by dilute sulphuric acid.

Benzaldehyde-*p*-tolylhydrazone therefore decomposes in a precisely similar manner to benzaldehydephenylhydrazone when heated. The greater part decomposes into benzylidene-*p*-toluidine, nitrogen, and ammonia, thus:

$$3CHPh{:}N{\cdot}NH{\cdot}C_6H_4Me = 3CHPh{:}N{\cdot}C_6H_4Me + N_2 + NH_3,$$

while a considerable but smaller fraction yields stilbene, nitrogen, and toluene, thus:

$$2CHPh{:}N{\cdot}NH{\cdot}C_6H_4Me = CHPh{:}CHPh + 2N_2 + 2C_6H_5Me.$$

Benzaldehyde-*o*-tolylhydrazone decomposes similarly when heated.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

CCXXI.—*The Absorption Spectra of Triketohydrindene Hydrate and Certain Derivatives.*

By JOHN EDWARD PURVIS.

THE absorption spectra of a series of coloured diketopyrrolines have been described and discussed by the author (Trans., 1910, **97**, 2535), and also of some derivatives and isomerides of 1 : 2-diketo-Δ^3-*cyclo*pentene (this vol., p. 107).

A series of coloured substances has been described by Ruhemann (Trans., 1910, **97**, 1438; this vol., p. 1486), and obtained from triketohydrindene hydrate, $C_6H_4{<}{}^{CO}_{CO}{>}C(OH)_2$, which from its

chemical behaviour was found to resemble alloxan very closely. These substances have been studied spectroscopically by the author in order to see how far the colour and absorption is connected (1) with the ketonic constitution, and (2) how far the colour and absorption are modified when the oxygen of the ketonic groups is replaced by other radicle groups. From chemical considerations, Ruhemann ascribed the following constitutional formulæ to the various compounds:

A. Triketohydrindene hydrate, $C_6H_4<\substack{CO\\CO}>C(OH)_2$, colourless.

B. Diphenylhydrazone of triketohydrindene, $\begin{matrix}C_6H_4\cdot C{:}N\cdot NHPh\\ \vert \qquad \vert \\ CO—C{:}N\cdot NHPh\end{matrix}$, red.

C. The hydrate of 2:3-bis-(*p*-dimethylaminoanilo)-*α*-hydrindone, $\begin{matrix}C_6H_4\cdot C{:}N\cdot C_6H_4\cdot NMe_2\\ \vert \qquad \vert \\ CO—C{:}N\cdot C_6H_4\cdot NMe_2\end{matrix}$, H_2O, very dark purple.

D. Ketohydrindenophenazine, $\begin{matrix}C_6H_4\cdot C{:}N\\ \vert \qquad \vert \\ CO—C{:}N\end{matrix}>C_6H_4$, canary-yellow.

E. 2-*o*-Carboxybenzoylindonoglyoxaline,

$$\begin{matrix}C_6H_4\cdot C\cdot NH\\ \vert \qquad \Vert \\ CO—C—N\end{matrix}\!\!>C\cdot CO\cdot C_6H_4\cdot CO_2H,$$

carmine-red.

F. 1:3-Diketohydrindamine, $C_6H_4<\substack{CO\\CO}>CH\cdot NH_2$, yellow; this substance was not obtained very pure, as it rapidly decomposed.

G. 1:3-Diketo-2-benzylidenehydrindamine,

$$C_6H_4<\substack{CO\\CO}>CH\cdot N{:}CHPh,$$

dull orange.

H. 1:3-Diketo-2-anisylidenehydrindamine,

$$C_6H_4<\substack{CO\\CO}>CH\cdot N{:}CH\cdot C_6H_4\cdot OMe,$$

vermilion-orange.

I. 1:3-Diketo-2-*p*-dimethylaminobenzylidenehydrindamine,

$$C_6H_4<\substack{CO\\CO}>CH\cdot N{:}CH\cdot C_6H_4\cdot NMe_2,$$

maroon or very dark red.

K. Diketohydrindylidenediketohydrindamine,

$$C_6H_4<\substack{CO\\CO}>CH\cdot N{:}C<\substack{CO\\CO}>C_6H_4,$$

deep red.

L. The ammonium salt of *K*,

$$C_6H_4<\substack{—CO—\\C(ONH_4)}>C\cdot N{:}C<\substack{CO\\CO}>C_6H_4,$$

deep red.

The substances A, B, C, D, and E were stable in absolute alcohol, although they differed greatly in their relative solubilities. The substances G, H, I, K, and L were very unstable in alcohol, but they were more stable in glacial acetic acid, and they were investigated when dissolved in that acid. The substance F decomposes so rapidly that no observations could be taken. Solutions of the various substances in milligram-molecules by weight were dissolved either in cold absolute alcohol or in glacial acetic acid, and their absorption spectra were examined photographically in the usual way, using Wratten and Wainwright's pan-chromatic plates. For example, $M/100$-solution means that one milligram-molecule by weight of the substance was dissolved in 100 c.c. of cold absolute alcohol or of glacial acetic acid, and this was further diluted so that 1000 c.c. contained one milligram-molecule by weight or $M/1000$-strength; and this again was diluted, so that it became $M/10,000$-strength. The absorption curves of the various solutions have been drawn. It will be seen that the colourless compound A has a well-marked band in $M/100$-solution (Fig. 1), the position of which is near the more refrangible end of the visible spectrum. The head of this band is at about 2800 (oscillation frequencies). $M/1000$-Solutions were also examined, but no other band was observed. The positions, the general absorption of which began through the following thicknesses of $M/1000$-solutions, were:

	λ.	$1/\lambda$.
3 mm. thickness	2480	4031
10 ,, ,,	2655	3765
30 ,, ,,	2775	3603
60 ,, ,,	2995	3338

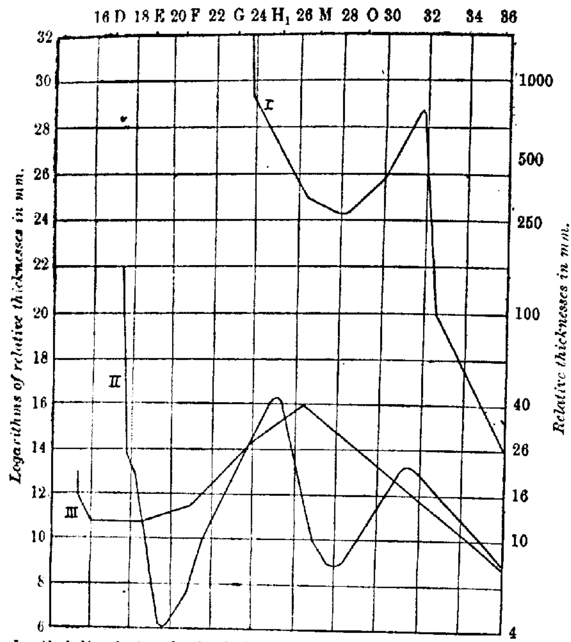
The substance B, the red diphenylhydrazone of triketohydrindene, was examined in $M/10,000$-solution, and showed two bands, the curves of which have been drawn (Fig. 1, II). The heads of these two bands are at 2800 and 1980. The more refrangible band, 2800, corresponds with the band found in triketohydrindene.

The substance C, a very dark purple, almost black, compound, which gives a very dark purple solution, was also investigated in a $M/10,000$-solution. When examined through a thickness of 24 mm. the solution was so dark that little or no light passed through. It will be seen from the curve (Fig. 1, III) that the two bands of the B compound have been fused into one large, not very persistent band, the head of which is at about 1900.

The general effect, therefore, of the substitution of the oxygen of two of the ketonic groups of the colourless compound A by complex aromatic nitrogen compounds is to damp the vibrations so that there is absorption of light within the visible regions of the

spectrum, and a characteristic colour is produced. The substances *D* and *E* were also examined, but in neither case was a band observed. The positions when general absorption began through

FIG. 1.



I. *Alcoholic solution of triketohydrindene hydrate* (A).
II. ,, ,, *diphenylhydrazone of triketohydrindene hydrate* (B).
III. ,, ,, *the hydrate of* 2 : 3-*bis*-(p-*dimethylaminoanilo*)-α-*hydrindone* (C).

the following thicknesses of $M/10,000$-alcoholic solutions of the substance *D* were:

	λ.	1/λ.
9 mm. thickness	3080	3244
30 ,, ,,	3300	3028
51 ,, ,,	3510	2848
90 ,, ,,	3930	2543
135 ,, ,,	4200	2380

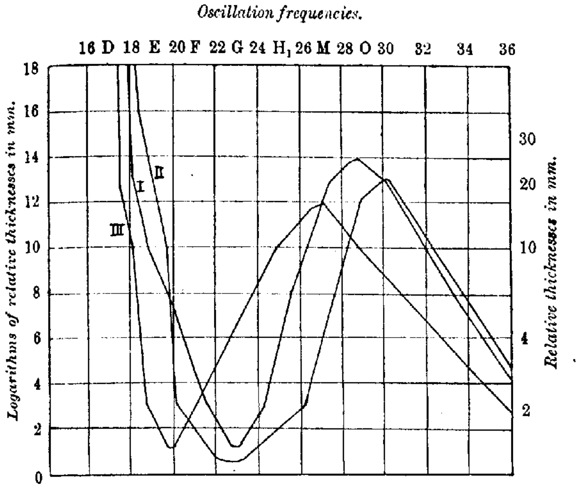
The positions when general absorption began through the following thicknesses of $M/10,000$-alcoholic solution of the substance *E* were:

	λ.	1/λ.
9 mm. thickness	2780	3595
30 ,, ,,	3580	2791
51 ,, ,,	3780	2644
90 ,, ,,	3880	2576
134 ,, ,,	4125	2433
146 ,, ,,	4150	2409

Stronger solutions of D and E were not obtained, as the substances were not easily soluble.

The explanation of these phenomena appears to be that the

FIG. 2.



I. *Acetic acid solution of* 1 : 3-*diketo-2-benzylidenehydrindamine* (G).
II. ,, ,, 1 : 3-*diketo-2-anisylidenehydrindamine* (H).
III. ,, ,, 1 : 3-*diketo-2-p-dimethylaminobenzylidenehydrindamine* (I).

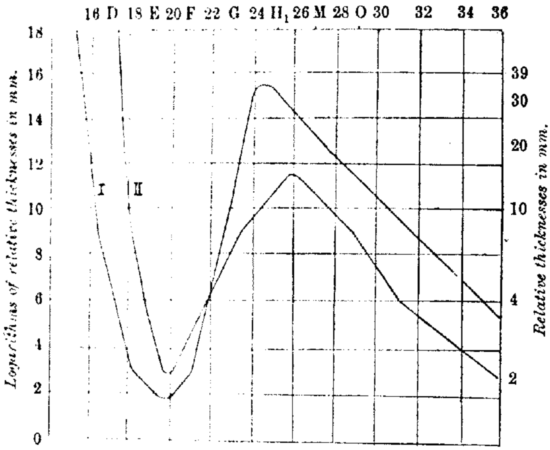
establishment of another ring in each of these compounds has destroyed the selective absorption exhibited by the compounds A, B, and C, and that the colour is produced by an extension of the general absorption within the regions of the visible parts of the spectrum.

The coloured compounds G, H, and I were examined in $M/1000$-solutions of glacial acetic acid, and the absorption curve of the band of each substance has been drawn (Fig. 2). It is evident from a study of these curves that the bands are all of the same type. The differences correspond with differences in the

shades of colour of the different compounds. For example, the substance G is a dull orange colour; the substance H a vermilion-orange; and the substance I is a maroon or a very dark red. The position of the bands, as well as their extension, illustrates these differences in shades of colour. The head of the band G is at about 2300; that of H is at about 2300, but is much wider than G; and that of I is about 2000. $M/10,000$-Solutions in glacial acetic acid were also examined through varying thicknesses, but no bands were observed in the ultra-violet regions.

FIG. 3.

Oscillation frequencies.



I. *Acetic acid solution of diketohydrindylidenediketohydrindamine* (K).
II. ,, ,, *the ammonium salt of diketohydrindylidene-diketohydrindamine* (L).

The substances K and L were also examined in $M/1000$-solutions of glacial acetic acid, and the absorption curve of each has been drawn (Fig. 3). Here, again, the bands are evidently of the same type, and the differences correspond with differences in the shades of colour, which are both dark purple-brown. The curve of the ammonium compound (L) is not so persistent as that of the parent substance (K). The head of the band of K is at about 1990, and that of L at about 2000. $M/10,000$-Solutions in acetic acid were also examined through varying thicknesses, but no bands were

observed in the ultra-violet regions. The positions where general absorption began in $M/10{,}000$-solutions were:

			λ.	1/λ.
K.	10 mm. thickness		2810	3556
	2 ,,	,,	2490	4014
L.	10 ,,	,,	2700	3702
	2 ,,	,,	2465	4054

So that the general effect of the substitution of oxygen in one of the ketonic groups of the colourless compound *A*, by complex aromatic compounds, is to damp the vibrations so that there is a selective absorption of light within the visible regions of the spectrum, and a characteristic colour is produced.

General Conclusions.

The results of the observations show that (1) the colour of the compounds is intimately connected with the presence of ketonic groups, phenomena which are analogous to those of the diketopyrrolines and the *cyclo*pentenes (*loc. cit.*); (2) the shade of colour is modified according to the type of the substituting groups; (3) where another ring is established, as in the compounds *D* and *E*, there is no selective absorption, and the colour is produced by an extension of the general absorption within the regions of the visible spectrum.

It is important to refer to the observations of Hartley (Trans., 1887, **51**, 154; 1905, **87**, 1791 *et seq.*), in which he shows that the colourless alloxan and uramil have no absorption bands, whereas the coloured murexide has two, the heads of which are at about 3300 and 1900; that is, the former, a weak band, is in the ultra-violet, and the latter, a strong and persistent one, is in the visible parts of the spectrum. These three compounds are constitutionally comparable with the compounds *A*, *F*, and *L* respectively. The comparison may be further extended in that the parent substance *A* (triketohydrindene hydrate) has no colour, although it exhibits an absorption band just beyond the visible part of the spectrum; the unstable substance *F* (1:3-diketohydrindamine) would probably show a similar band; and the coloured substance *L* (the ammonium salt of diketohydrindylidenediketohydrindamine) exhibits a band in the visible regions of the spectrum.

Apart from this comparison, it is also clear that selective absorption need not accompany the phenomenon of colour, as the author has shown in the isomerides of *cyclo*pentene (*loc. cit.*); and the observation is confirmed by the coloured compounds *D* and *E* of this investigation, where no selective absorption was found.

Although there is no selective absorption, it is probable that the colour is the result of the transmission of rays between definite regions, the limit of which, in one direction, extends into the infra-red; and there is every possibility that such compounds would show selective absorption in these regions.

I have again to thank the Government Grant Committee of the Royal Society, by whose assistance the spectroscope was obtained; and also Dr. Ruhemann for pure specimens of the substances examined.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCXXII.—*The Alkaline Condensations of Nitro-hydrazo-compounds. Part I.*

By ARTHUR GEORGE GREEN and ERNEST ARTHUR BEARDER.

IN a series of researches on the constitution of the stilbene dyestuffs conducted by Green and former collaborators (Trans., 1904, **85**, 1424, 1432; 1906, **89**, 1602; 1907, **91**, 2076; 1908, **93**, 1721), it has been shown that the production of azostilbene compounds, whether by alkaline condensation of derivatives of *p*-nitrotoluene or by alkaline reduction of derivatives of 4:4′-dinitrostilbene, is preceded by the formation of unstable intermediate products, to which the constitution of nitrosostilbenes was assigned.

In view of the parallelism between the ·N:N· and ·CH:CH· series which is exhibited in the following, amongst other, reactions:

$$\underset{p\text{-Nitrotoluene.}}{H_3C{\cdot}C_6H_4{\cdot}NO_2} \xrightarrow[\text{hypochlorites}]{\text{Oxidation with}} \underset{4:4'\text{-Dinitrostilbene.}}{NO_2{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO_2}$$

$$\underset{p\text{-Nitroaniline.}}{H_2N{\cdot}C_6H_4{\cdot}NO_2} \xrightarrow[\text{hypochlorites}]{\text{Oxidation with}} \underset{4:4'\text{-Dinitroazobenzene.}}{NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NO_2}$$

it seemed not improbable that condensations might occur in the azo-series similar to those which give rise to the stilbene dyestuffs. It has long been known that by partial reduction of 4:4′-dinitro-azobenzene a product is obtained which dissolves in alkali hydroxides with an intense blue colour, and it appeared possible that an analogy might exist between this product and the above-mentioned intermediate compounds of the stilbene class, which dissolve in alkalis with a crimson to blue colour. This anticipation was strengthened when we found that the former substance exhibited

its general behaviour a remarkable similarity to the latter class of compounds. Thus, in alkaline solution both are readily decolorised by air, the former yielding dinitroazobenzene, the latter dinitrostilbene. On heating their alkaline solutions, both are finally converted into stable yellow condensation products, which dissolve in concentrated sulphuric acid with a similar cherry-red colour. Further, in both cases these stable condensation products are converted by alkaline reducing agents into other products dissolving in concentrated sulphuric acid with a blue colour.

Assuming that the intermediate products of the stilbene condensation are correctly regarded as nitroso-compounds, the existence of a series of parallel condensations in the azo-class would necessitate the conclusion, either that the above reduction product of dinitroazobenzene, which is usually regarded as dinitrohydrazobenzene, is actually a nitroso-compound, or that such a nitroso-compound is formed in an early stage of its alkaline condensation. The present research has been undertaken with the object of investigating these questions, and, incidentally, of obtaining further light on the course of the stilbene reactions.

The product of the partial reduction of 4:4′-dinitroazobenzene, which dissolves with a bright blue colour in aqueous alkalis, has already been the subject of frequent investigations, which have led to very divergent views as to its constitution. It was discovered by Lermontoff in 1872 (*Ber.*, 1872, **5**, 232), who regarded it as a dinitrohydrazobenzene, $N_2H_2(C_6H_4{\cdot}NO_2)_2$, a conclusion which was strongly supported later by the work of Werner and Stiasny (*Ber.*, 1899, **32**, 3272). On the other hand, Janovsky (*Monatsh.*, 1885, **6**, 160), whose analytical results differ widely from those of other authors, ascribes to the compound the constitution of a nitrolic acid, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(OH){\cdot}N(OH){\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2$. Willgerodt (*J. pr. Chem.*, 1890, [ii], **42**, 51) regards it as an "azhydroxyazo" compound, $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NH(OH){:}O$; whilst Freundler and Beranger (*Compt. rend.*, 1902, **134**, 1219) support the quinonoid formula: $HO_2N{:}C_6H_4{:}N{\cdot}N{:}C_6H_4{:}NO_2H$. Another possible structure hitherto unconsidered is that of a hydrated dinitrosoazobenzene, $(HO)_2N{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}N(OH)_2$.

The preparation of this product at first offered some difficulties, owing to the absence of details in the published accounts, but it was finally obtained in a pure state and in good yield by reduction with colourless ammonium sulphide. When crystallised from acetone it had the characteristic crystalline form described by Janovsky, and after drying at 140° it melted (if heated quickly) at 228°, as given by Werner and Stiasny. The great variation in melting point observed by different investigators (L., 220°; J., 218°;

W., 248—250°; W. and S., 228°), which at first sight seems to suggest that they had varying products in hand, is more probably to be referred to the different rate of heating. The nitrogen value obtained for the compound agreed exactly with a dinitrohydrazobenzene, although it also approximated to the figure required for the hydrated dinitrosoazobenzene. On oxidising the blue alkaline solution by shaking with air or by addition of iodine, dinitroazobenzene was regenerated. Titration of the alkaline solution with a standard solution of iodine until complete disappearance of the blue colour, gave results which indicated the removal of two atoms of hydrogen. Titration of the acetic acid solution with titanium trichloride also gave figures in agreement with the dinitrohydrazobenzene formula, and this was further supported by the behaviour of the compound with acetic anhydride. When heated with this reagent for a short time only it remained unaltered, whereas if it were a hydrated form of dinitrosoazobenzene, or had the "azhydroxyazo" formula suggested by Willgerodt, it should lose the elements of water. When boiled with a large excess of acetic anhydride for two hours it was converted into a diacetyl derivative, melting at 188—189°, which is doubtless identical with the dinitrodiacetylhydrazobenzene (m. p. 186—187°) obtained by Freundler and Beranger by nitration of diacetylhydrazobenzene. There is thus no reason to doubt the correctness of the conclusion arrived at by Werner and Stiasny, that the reduction product is actually dinitrohydrazobenzene.

The question next arises whether the blue colour of the alkaline solution is due to the formation of a salt of dinitrohydrazobenzene or whether a molecular change occurs under the influence of the alkali.

To ascertain this, a series of experiments was conducted, in which weighed quantities of the dinitrohydrazobenzene were dissolved in cold aqueous sodium hydroxide (10 to 20 per cent. NaOH), and then filtered into aqueous acid, both solution and filtration being effected in an apparatus from which air was completely excluded by means of hydrogen. If intermolecular oxidation and reduction occurred, it was to be expected that a precipitate of dinitroazobenzene would be produced. The dinitrohydrazobenzene dissolved completely, and the deep blue liquid, when not allowed to remain for more than fifteen minutes, left no appreciable precipitate on the filter. We further found that the freshly prepared blue solution gave when immediately acidified a light yellow precipitate of unaltered dinitrohydrazobenzene. It must therefore be concluded that the blue compound actually represents an alkali salt of dinitrohydrazobenzene, and if its entirely different colour and

much greater oxidisability in comparison with the free compound be considered, the assumption seems justified that the latter is a pseudo-acid, giving rise to salts of the quinonoid type,

$$M'O\cdot ON{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}NO\cdot OM'.$$

This conclusion is also in agreement with the work of Grandmougin and Leeman (*Ber.*, 1906, **39**, 4384; 1908, **41**, 1295), who have isolated a blue dipotassium salt of hexanitrohydrazobenzene,

$$C_6H_2(NO_2)_3\cdot NH\cdot NH\cdot C_6H_2(NO_2)_3.$$

In the course of the above experiments it was observed that if the blue solution in aqueous sodium hydroxide (10 per cent. NaOH) is kept with exclusion of air for several hours, the colour becomes slightly more violet, whilst a small precipitation of dinitroazobenzene occurs. If the blue solution is now acidified, the precipitate has a much more orange colour than previously, is more voluminous, and is completely soluble in cold glacial acetic acid, in which dinitrohydrazobenzene scarcely dissolves at all. It also exhibits a much greater solubility in alcohol and in ether. In aqueous sodium hydroxide it dissolves readily with the same blue colour as dinitrohydrazobenzene, but, on the other hand, dissolves in sulphuric acid with a reddish-orange colour, in contrast to the pure yellow of the latter. When dry it forms a brick-red, amorphous powder, which could not be obtained crystalline. Analysis of this product gave numbers for carbon, hydrogen, and nitrogen conforming to dinitrohydrazobenzene, with which the results of titration with titanium trichloride were also in correspondence. If boiled, however, with acetic anhydride under conditions in which dinitrohydrazobenzene is quantitatively converted into the diacetyl derivative, the product in question gave rise to dinitroazobenzene (yield of about 70 per cent.). These results appeared at first sight to indicate that we had in hand a compound isomeric with the original dinitrohydrazobenzene. Such a supposition was, however, very difficult to express by any probable formula, and doubts arose as to its validity when it was found possible by repeated crystallisation from acetone to separate from the product a small quantity of pure dinitrohydrazobenzene. Subsequent experiments proved that the substance was in fact a mixture consisting of about four-fifths of unaltered dinitrohydrazobenzene with about one-fifth of a new compound. The latter was obtained pure by effecting the conversion with weaker alkali (3 per cent. NaOH), and allowing the solution to remain at the summer temperature (about 25°) for from six to sixteen hours. A violet-blue solution was thus produced, in which was suspended a considerable amount of dinitroazobenzene. After filtration from the latter the blue solution was acidified with acetic acid, which produced a very voluminous, colloidal, orange-red

precipitate. By rapid crystallisation from acetone the new compound was obtained in small, red cubes with a violet reflex. In concentrated sulphuric acid it dissolved with a pure crimson colour, which on addition of a drop of dilute nitric acid was changed to yellow (formation of dinitroazobenzene). It dissolved in alkali hydroxides to a violet-blue solution, which, like that of dinitrohydrazobenzene, is decolorised by air or iodine. A determination of the relative quantities of the new compound and of dinitroazobenzene produced from a given weight of dinitrohydrazobenzene gave results in agreement with the supposition that the reaction proceeds according to one or other of the two following equations:

$$(a)\ 2NO_2\cdot C_6H_4\cdot N_2H_2\cdot C_6H_4\cdot NO_2 = NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NO_2 + C_{12}H_{10}O_3N_4 + H_2O.$$

$$(b)\ 2NO_2\cdot C_6H_4\cdot N_2H_2\cdot C_6H_4\cdot NO_2 = NO_2\cdot C_6H_4\cdot N_2\cdot C_6H_4\cdot NO_2 + C_{12}H_8O_2N_4 + 2H_2O.$$

The estimation of carbon, hydrogen, and nitrogen, and the results obtained by titration with titanium trichloride, establish for the compound the constitution $C_{12}H_{10}O_3N_4$; it is therefore formed in accordance with the first equation. The substance is therefore either a 4-nitro-4′-nitrosohydrazobenzene,

$$NO\cdot C_6H_4\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2,$$

or a hydrated 4 : 4′-dinitrosoazobenzene,

$$NO\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot N(OH)_2.$$

As, however, the titration of the alkaline solution with standard iodine indicates the loss of two atoms of hydrogen in a similar manner to dinitrohydrazobenzene, the first of these formulæ appears the more probable.

Accepting the conclusion that the free compound is nitronitrosohydrazobenzene, it is probable that its violet-blue alkaline solutions contain quinonoid salts of the constitution

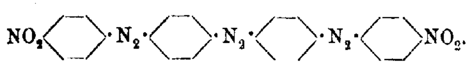
$$M'O\cdot ON{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}N\cdot OH.$$

These salts should be identical with the oxime corresponding with the red alkaline salts of *p*-nitrobenzeneazophenol, to which Hewitt assigns the formula $M'O\cdot ON{:}C_6H_4{:}N\cdot N{:}C_6H_4{:}O$. Attempts to prepare the former by the action of hydroxylamine on the latter have not, however, been successful.

In respect to the incomplete action of cold alkali hydroxides on dinitrohydrazobenzene, it was found by direct experiment that a mixture composed of one part of nitronitrosohydrazobenzene and four parts of dinitrohydrazobenzene, when precipitated together, exhibited exactly the same properties as the product at first supposed to be an isomeric dinitrohydrazobenzene. The orange colour in sulphuric acid, its colloidal properties, and much greater solubility in solvents are therefore all due to the admixture of

nitronitrosohydrazobenzene. The different behaviour of the product with acetic anhydride appears also to be referable to the same cause, for the nitroso-compound on account of its greater reducibility may effect oxidation of dinitrohydrazobenzene to dinitroazobenzene before acetylation can occur.

As mentioned above, the final product of the action of alkali hydroxides on dinitrohydrazobenzene is very analogous to the final product of the stilbene condensation. It was obtained by heating the solution of nitronitrosohydrazobenzene in 3 per cent. sodium hydroxide to 100° until complete disappearance of the blue colour (air being rigidly excluded). The orange-coloured precipitate, after crystallisation from xylene, was obtained in sparingly soluble, orange needles, melting at 285—286°. Analysis supported the constitution:



The compound is therefore a *bisnitrobenzeneazo-azobenzene*, and owes its formation to the condensation of two molecules of nitronitrosohydrazobenzene, in accordance with the scheme:

$$NO_2{\cdot}C_6H_4{\cdot}\overset{H}{N}{\cdot}\overset{H}{N}{\cdot}C_6H_4{\cdot}\overset{O}{N} \longrightarrow \longleftarrow \overset{O}{N}{\cdot}C_6H_4{\cdot}\overset{H}{N}{\cdot}\overset{H}{N}{\cdot}C_6H_4{\cdot}NO_2$$

In preparing the compound it is not necessary to employ the isolated nitronitrosohydrazobenzene, but the blue alkaline solution of dinitrohydrazobenzene may be heated at once to 100° until the blue colour disappears. The orange precipitate then obtained is a mixture of bisnitrobenzeneazo-azobenzene with dinitroazobenzene, and can be readily separated by solvents, in which the former compound is much less soluble. A quantitative determination of the yield of the two products agreed with the equation:

$$4NO_2{\cdot}C_6H_4{\cdot}N_2H_2{\cdot}C_6H_4{\cdot}NO_2 = 2NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2 + C_{24}H_{16}O_4N_8 + 4H_2O.$$

It was further found that the condensation of nitronitrosohydrazobenzene to bisnitrobenzeneazo-azobenzene can also be effected by merely boiling the former with neutral solvents.

The above experiments fully justify our original expectation of the existence of a parallelism between the derivatives of dinitroazobenzene and those of dinitrostilbene. If this analogy is complete it would seem to suggest that the intermediate products of the stilbene reaction are not, as hitherto believed, dinitrosostilbenes, $NO{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}C_6H_4{\cdot}NO$, but rather nitronitrosodibenzyls,

$$NO{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH_2{\cdot}C_6H_4{\cdot}NO_2,$$

from which the final condensation products (stilbene dyestuffs) are formed in the manner indicated above for bisnitrobenzeneazo-azo-

benzene. The mobility of the two methylene hydrogen atoms may very probably be connected with the tendency to form quinonoid salts. The chief difficulty in this view lies in the fact that coloured (blue?) quinonoid salts of dinitrodibenzyl,

$$M'O\cdot ON:C_6H_4:CH\cdot CH:C_6H_4:NO\cdot OM',$$

corresponding with the blue quinonoid salts of dinitrohydrazobenzene, have hitherto not been observed. The dinitrodibenzyl salts and those of its derivatives which have been investigated all give no colour with alkali hydroxides, except on heating. It is, however, possible that owing to the firmer attachment of hydrogen to carbon compared with that of hydrogen to nitrogen, the formation of quinonoid salts may take place with greater difficulty, or only at temperatures at which conversion into the nitronitroso-compound follows immediately. This is supported to some extent by the observation made by Green and Wahl, that dinitrodibenzyl-disulphonic acid when heated with sodium hydroxide is converted, in the first instance, into a mixture of dinitrostilbenedisulphonic acid with the crimson intermediate product. If the latter is nitronitrosodibenzyldisulphonic acid, the reaction is exactly analogous to the above-described formation of dinitroazobenzene and nitronitrosohydrazobenzene from two molecular proportions of dinitrohydrazobenzene, and just as in this case may be preceded and conditioned by the prior formation of a quinonoid salt.

EXPERIMENTAL.

4 : 4'-*Dinitroazobenzene.*

This compound was prepared both by nitration of azobenzene and by oxidation of *p*-nitroaniline with calcium hypochlorite, identical products being obtained in both cases. The latter method, by which the pure product can readily be obtained in quantity, was that finally adopted. In conformity with Meigen and Normann (*Ber.*, 1900, **33**, 2711), we found that the product of this reaction is the azo- and not the azoxy-compound. The operation is best conducted in the following manner: One hundred grams of *p*-nitroaniline are dissolved in a mixture of hydrochloric acid and hot water, filtered through glass wool, and poured into about $2\frac{1}{2}$ litres of cold water, the base being thus obtained in a fine state of division. The mixture is then rendered alkaline with sodium hydroxide, and a clear solution of calcium hypochlorite added, containing about 50 per cent. more chlorine than that theoretically required. After stirring for about six hours and leaving overnight, the orange precipitate is collected, washed well with cold water, and then without drying extracted on the filter with cold acetone,

in order to remove unaltered *p*-nitroaniline and dark-coloured by-products. The residue is recrystallised from boiling xylene, from which it separates in long, orange-red leaflets, melting at 222—223°. To facilitate the subsequent reduction, it was found very advantageous to convert the product into a fine state of division by dissolving it in cold concentrated sulphuric acid, and pouring into water. In this case it is not necessary to crystallise from xylene, and the purification with acetone may be conveniently replaced by an extraction with cold dilute hydrochloric acid to remove *p*-nitroaniline, calcium carbonate, and other impurities. (Found, N=20·87. Calc., N=20·59 per cent.)

4:4′-*Dinitrohydrazobenzene*, $NO_2\cdot C_6H_4\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$.

After a number of experiments with various alkaline reducing agents, such as zinc dust and sodium hydroxide, dextrose and alkali, sodium sulphide, yellow ammonium sulphide, etc., none of which gave good results, the following method of preparation with colourless ammonium sulphide was adopted. The reagent was prepared just before use by saturating a mixture of equal parts of concentrated aqueous ammonia and water with hydrogen sulphide. Eleven grams of finely divided dinitroazobenzene are mixed in a mortar to a uniform paste with 150 c.c. of 95 per cent. alcohol, to which a few c.c. of acetone are added. The paste is transferred to a flask, heated to boiling, and 100 c.c. of the above aqueous ammonium sulphide are brought in. An immediate reaction occurs, and after about two minutes' boiling an equal volume of cold water is added. After cooling, the yellow precipitate is collected, washed with hot water, and then with alcohol, after which it is extracted with chloroform to remove any sulphur that may be present. The product is then dissolved in about 300 c.c. of boiling acetone (to which a little alcohol is added), and on cooling dinitrohydrazobenzene separates in pale yellow, transparent, rhombic prisms. The product on drying at 140° loses acetone, becoming opaque and of a deeper yellow colour. The yield was 6 or 7 grams. The product dried at 140° was found to melt at 228° if heated quickly, but on slower heating it melted at various other temperatures up to 250°. (Found, N=20·4. Calc., N=20·4 per cent.)

Reduction in acetic acid solution with standard titanium trichloride, titrating back the excess with ferric alum, gave the following result:

Hydrogen used=5·08, 5·27, 5·17.

Hydrogen theoretically necessary for reduction of dinitrohydrazobenzene to *p*-phenylenediamine=5·11 per cent.

In order to estimate the quantity of oxygen required to effect

decolorisation of the alkaline solution, titration with standard iodine in an atmosphere of hydrogen was employed. The end-point, indicated by the disappearance of the blue colour, is sharply defined. To secure rapid solution of the dinitrohydrazobenzene in the dilute sodium hydroxide employed and thus avoid any condensation, it was found advisable previously to dissolve the compound in acetone, reprecipitate with water, and wash thoroughly until every trace of acetone was removed. The fine precipitate was then transferred to a closed flask with 50 c.c. of water, the air displaced by hydrogen, and 50 c.c. of 6 per cent. sodium hydroxide were introduced from a tap funnel. Titration is then effected with $N/20$-iodine immediately solution has occurred:

Oxygen consumed = 6·3 and 5·96.

Oxygen required to oxidise dinitrohydrazobenzene to dinitroazobenzene = 5·79 per cent.

Dinitrodiacetylhydrazobenzene, $NO_2{\cdot}C_6H_4{\cdot}NAc{\cdot}NAc{\cdot}C_6H_4{\cdot}NO_2$.

One gram of dinitrohydrazobenzene was boiled for two hours with 20 c.c. of acetic anhydride, air being excluded. After evaporating off the excess of acetic anhydride, the mass was extracted with cold chloroform, and the residue crystallised from boiling glacial acetic acid. The product separated in colourless plates, which melted at 188—189°. It was insoluble in cold alkali hydroxides, but on boiling gave the deep blue colour of dinitrohydrazobenzene. (Found, N = 15·81. Calc., N = 15·64 per cent.)

4 : 4′-*Nitronitrosohydrazobenzene*, $NO{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2$.

This compound constitutes the first stage of the action of alkali hydroxides on dinitrohydrazobenzene. The best conditions for obtaining it in a pure state free from unconverted dinitrohydrazobenzene and from the bisnitrobenzeneazo-azobenzene produced by further condensation were only ascertained after a long series of experiments. Although the condensation commences almost immediately, the rate of the reaction is dependent on the temperature of the solution and its concentration in alkali hydroxide; thus with sodium hydroxide solutions of from 10 to 20 per cent. the reaction is much slower than with solutions of only 3 per cent. With solutions of the former strength and at a temperature of about 15° we obtained colloidal mixtures, in which dinitrohydrazobenzene largely preponderated, but which, nevertheless, exhibited very different properties from the latter in the pure state (see introduction). It was finally ascertained that a complete conversion into

he nitronitroso-compound, without any further condensation, is effected by allowing dinitrohydrazobenzene dissolved in eighty parts of 3 per cent. sodium hydroxide to remain at 25° (laboratory summer temperature) for from six to sixteen hours. The operation is best carried out in a bottle provided with a well-fitting, greased stopper, and nearly filled in order to exclude air. The progress of the reaction can be followed by precipitating at intervals small samples of the filtered solution with acetic acid, and dissolving the precipitate in concentrated sulphuric acid. After only a minute or two the solution in sulphuric acid is pure yellow (unaltered dinitrohydrazobenzene), after ten minutes it is reddish-orange, after half an hour red, and after five hours pure crimson, whilst after sixteen hours no further change is visible. When this point is reached the violet-blue solution is filtered quickly from precipitated dinitroazobenzene, and the filtrate allowed to run directly into an excess of dilute acetic acid. The product was a highly voluminous, gelatinous, reddish-orange precipitate, readily soluble in cold glacial acetic acid, acetone, ether, etc. It was washed thoroughly with water, pressed, dried at the ordinary temperature, and dissolved in acetone. On quickly evaporating the acetone the compound crystallised in small, orange-red cubes with a violet reflex. It is necessary to work quickly in order to avoid condensation of the nitronitroso-compound to bisnitrobenzeneazo-azobenzene. *Nitronitrosohydrazobenzene* is readily soluble in solvents such as acetone, alcohol, ether, acetic acid, but sparingly so in hydrocarbons. The solution in acetone has a deep yellow colour, which was found to be about forty times as intense as a similar solution of dinitrohydrazobenzene. The substance has pronounced tinctorial properties, dyeing silk from an aqueous alcoholic solution in red shades, which are changed to blue by immersion in dilute sodium hydroxide. It has no definite melting point, but begins to decompose at about 203°. Its alkali hydroxide solution has a more violet tint of blue than that of dinitrohydrazobenzene. Like the latter it is decolorised by air or iodine. In addition to its acid properties the compound appears also to be a weak base, giving pink solutions with aqueous acids. It dissolves in concentrated sulphuric acid with a pure crimson colour, which is changed to pure yellow (dinitroazobenzene) on adding a drop of dilute nitric acid.

On account of its instability the compound was analysed in the air-dried condition, the percentage of moisture it contained being determined simultaneously by drying at 140°, and the correction introduced:

0·0967 * gave 0·1990 CO_2 and 0·0348 H_2O. C=56·05; H=3·95.
0·0964 * „ 0·1992 CO_2 „ 0·0367 H_2O. C=56·34; H=4·22.
0·0950 * „ 0·1917 CO_2 „ 0·0355 H_2O. C=55·1; H=4·1.
0·0991 * „ 19·6 c.c. N_2 at 25° and 757·5 mm. N=22·64.
0·1006 * „ 19·9 c.c. N_2 „ 26·5° „ 760·3 mm. N=22·73.
0·0913 * „ 18·3 c.c. N_2 „ 23° „ 754 mm. N=22·73.
Mean: C=55·83; H=4·09; N=22·7.

$C_{12}H_{10}O_3N_4$ requires C=55·67; H=3·91; N=21·7 per cent.

Reduction in a boiling acetic acid solution with a standard solution of titanium trichloride gave the following results:

Hydrogen consumed=5·36 and 5·06.

Hydrogen required for reduction to *p*-phenylenediamine=4·70 per cent.

Titration of the alkaline solution with standard iodine in an atmosphere of hydrogen (in the manner described above, but without previously dissolving in acetone) gave the following results:

Oxygen consumed=5·55 and 5·53.

Oxygen required to oxidise nitronitrosohydrazobenzene to nitronitrosoazobenzene=6·15 per cent.

Attempts to isolate nitronitrosoazobenzene from the orange-yellow precipitate formed in this reaction proved unsuccessful, the nitroso-compound apparently undergoing further condensation in the alkaline medium or during subsequent purification.

The conclusion based on the above analyses, that under the influence of alkali hydroxides two molecular proportions of dinitrohydrazobenzene give rise to one of nitronitrosohydrazobenzene and one of dinitroazobenzene, was further supported by the following quantitative experiments:

A. 3·75 Dinitrohydrazobenzene gave 1·632 nitronitrosohydrazobenzene and 1·879 dinitroazobenzene. The quantities theoretically required are 1·765 of the former and 1·861 of the latter.

B. A solution of 0·0522 dinitrohydrazobenzene in 3 per cent. sodium hydroxide was allowed to remain for five hours at 25°, air being carefully excluded by means of hydrogen. At the end of this time the solution was titrated with standard iodine (in absence of air) until the disappearance of the blue colour.

The iodine required was equivalent to 0·00132 gram of oxygen.

Percentage of oxygen consumed=2·5, that is, approximately half the quantity (5·79) which would have been required had the solution been titrated immediately.

* Dry.

Bisnitrobenzeneazo-azobenzene,
$NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_4 \cdot NO_2$.

This substance is readily formed by further condensation of nitronitrosohydrazobenzene, either by heating the alkaline solution or by boiling the substance itself with neutral solvents. In place of employing nitronitrosohydrazobenzene itself, the alkaline solution of dinitrohydrazobenzene may be directly heated, in which case dinitroazobenzene is formed simultaneously.

I. Finely powdered nitronitrosohydrazobenzene was placed in a well-stoppered bottle filled with about fifty parts of aqueous 3 per cent. sodium hydroxide, and heated in boiling water until the blue colour had entirely disappeared, leaving a red liquid, in which was suspended a bright orange precipitate. The time of heating required was about four hours. The orange precipitate was collected, well washed with water, and dried. The crude product was almost pure, and melted at about 285°. It contained no dinitroazobenzene.

II. About $1\frac{1}{2}$ grams of dinitrohydrazobenzene were heated as above with 70 c.c. of aqueous 3 per cent. sodium hydroxide. When the conversion was complete, the precipitate was collected, washed, and dried. It was then boiled with glacial acetic acid, which dissolved about half the whole, and on cooling deposited dinitroazobenzene in the characteristic orange plates, melting at 222·5—223°. The insoluble residue was dissolved in a large volume of boiling solvent-naphtha, from which after filtration and cooling bisnitrobenzeneazo-azobenzene crystallised in very small, brownish-orange needles, melting at 285—286°.

III. 0·1748 Gram of nitronitrosohydrazobenzene was boiled with 50 c.c. of solvent naphtha until it dissolved completely (about six hours' boiling were necessary). The solution was concentrated to about half its volume, and allowed to cool, when the condensation product crystallised out in microscopic, orange-brown needles, which melted at 284—285°. The yield was 0·1042 gram, the conversion being complete.

For analysis the substance was dried at 140°:

0·0923 gave 0·2022 CO_2 and 0·0297 H_2O. C=59·74; H=3·57.
0·0863 „ 16·6 c.c. N_2 at 30·5° and 773 mm. N=22·2.
0·0718 „ 14 c.c. N_2 at 28° and 767 mm. N=22·5.
$C_{24}H_{16}O_4N_8$ requires C=60·0; H=3·33; N=23·3 per cent.

This constitution is further supported by a determination of the relative quantity of condensation product and dinitroazobenzene produced from a given weight of dinitrohydrazobenzene:

0·9024 dinitrohydrazobenzene gave 0·4531 bisnitrobenzeneazo-azobenzene and 0·4372 dinitroazobenzene. This approximates very closely to that theoretically required.

Bisnitrobenzeneazo-azobenzene crystallises in very small, orange needles or leaflets, and is very sparingly soluble in all solvents. Its concentrated sulphuric acid solution is cherry-red, which becomes more crimson on addition of a small quantity of water, and is not decolorised by a drop of dilute nitric acid (distinction from the nitronitroso-compound). Alkaline reducing agents convert it into a compound which dissolves in concentrated sulphuric acid with a blue colour, and the investigation of which is at present proceeding.

DEPARTMENT OF TINCTORIAL CHEMISTRY,
UNIVERSITY, LEEDS.

CCXXIII.—*Trimercuridiethylammonium Nitrite.*

By PRAFULLA CHANDRA RÂY and JITENDRA NATH RAKSHIT.

IT is well known that when a solution of mercuric chloride is treated with ammonia, the so-called infusible white precipitate is obtained, to which the formula $NHg''H_2Cl$ has been assigned. One of us has shown that the interaction of mercuric nitrite and aqueous ammonia gives rise to dimercuriammonium nitrite, $NHg_2''NO_2$ (Trans., 1902, **81**, 645). This compound may be regarded as ammonium nitrite, in which the four atoms of hydrogen have been displaced by two atoms of dyad mercury. If mercuric chloride is acted on by ethylamine instead of ammonia, the alkyl substituted compound, $NHg''EtHCl$, is, as might be expected, the product of reaction.

We treated a solution of mercuric nitrite with methylamine with a view to ascertain if the formation of a corresponding alkyl derivative takes place. Although we failed to obtain the expected compound, dimercuriammonium nitrite being the product, an examination of the filtrate led to the isolation of methylammonium nitrite (this vol., p. 1016). Reference has already been made to the fact that, by the interaction of ethylamine and mercuric nitrite, not only dimercuriammonium nitrite, but also the alkyl substituted compound, trimercuridiethylammonium nitrite, $N_2Hg_3''Et_2(NO_2)_2$, is obtained (this vol., p. 1470). Ethylammonium nitrite, of course, remains in the filtrate.

Method of Preparation.—To a solution of mercuric-sodium nitrite is added an aqueous solution of ethylamine, taking care that the beaker is vigorously shaken after each addition. The reaction may

be taken as completed when the odour of ethylamine distinctly persists, even after a lapse of several minutes. The flocculent, heavy precipitate is washed by the aid of the pump, and dried in a steam-oven. The substance is perfectly white, whereas dimercuri-ammonium nitrite is pale yellow. In fact, by the physical difference in this property alone the one could be distinguished from the other. By a little practice the conditions which favour the formation of trimercuridiethylammonium nitrite to the exclusion of dimercuriammonium nitrite can be secured. The reaction evidently takes place according to the equations:

$$3\,Hg''(NO_2)_2 + 6NH_3Et{\cdot}OH = N_2Hg_3''Et_2(NO_2)_2 + 4NH_3Et{\cdot}NO_2 + 6H_2O \quad . \quad . \quad . \quad (1)$$

$$2\,Hg''(NO_2)_2 + 4NH_3Et{\cdot}OH = NHg_2''NO_2 + EtOH + 3NH_3Et{\cdot}NO_2 + 3H_2O \quad . \quad . \quad . \quad (2)$$

The substance dissolves readily in hydrochloric acid with the evolution of nitrous fumes.

Found: Hg = 75·30, 75·33; C = 6·24, 6·02; N = 7·30, 7·72.

$C_4H_{10}O_4N_4Hg_3,H_2O$ requires Hg = 75·37; C = 6·03; N = 7·04 per cent.

The hydrogen was not estimated owing to the risk of vapour of mercury entering into the calcium chloride tube, and thus vitiating the results. The salt evidently contains one molecule of water of crystallisation; this is quite in accord with the fact that dimercuri-ammonium nitrite, which is derived from a single molecule of ammonium nitrite, contains half a molecule of water.

The filtrate was subjected to distillation, and the presence of ethyl alcohol in the distillate was proved by the iodoform test; it was no doubt derived from the decomposition of the ethylammonium nitrite.

It is of interest to note that whilst by the action of ammonia and alkylated ammonia on mercuric chloride the compounds $NHg''H_2Cl$ and $NHg''EtHCl$ respectively are formed, with mercuric nitrite there are always obtained products in which all the atoms of hydrogen of ammonium nitrite are displaced by mercury and alkyl radicles.*

We are engaged in studying the action of other alkylated ammonias on mercuric nitrite.

Chemical Laboratory,
Presidency College, Calcutta.

* In this communication we have used the term dimercuriammonium nitrite in preference to dimercurammonium nitrite, as the former appears to be in strict conformity with scientific nomenclature.

CCXXIV.—*Studies of Ammonium Solutions. Part I. An Ammonium Electrode.**

By ROLAND EDGAR SLADE.

IT has been shown (Le Blanc, *Zeitsch. physikal. Chem.*, 1890, **5**, 467; Coehn, *Zeitsch. anorg. Chem.*, 1900, **25**, 430; Smith, *J. Amer. Chem. Soc.*, 1907, **29**, 844; see also McCoy and Moore, *ibid.*, 1911, **33**, 273) that ammonium, NH_4, behaves like a metal in that it is able to form an amalgam with mercury, and that NH_4 in this amalgam is able partly to displace sodium, potassium, and barium from aqueous solutions of their salts. From analogy it seemed probable that when ammonia and hydrogen were dissolved in platinum there would be some ammonium formed, and that there would be an equilibrium:

$$NH_3 + H \rightleftarrows NH_4$$

between ammonia, atomic hydrogen, and ammonium. It is known that hydrogen dissolved in platinum exists in the atomic state (Richardson, Nocol, and Parnell, *Phil. Mag.*, 1904, [vi], **8**, 1). If this equilibrium exists, a piece of platinised platinum saturated with hydrogen and ammonia would act as an ammonium electrode in a solution containing ammonium ions.

By Nernst's theory the potential, e, of this electrode would be:

$$e = -\frac{RT}{F}\ln\frac{k_1C}{c} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where: k is a constant.

C is the concentration of ammonium in the platinum.

c is the concentration of ammonium in the aqueous solution.

This potential will be that of the reaction:

$$2NH_3 + H_2 \longrightarrow 2NH_4^{\cdot} + 2\ominus,$$

and will vary with the partial pressures of NH_3 and H_2, and with the concentration of the ammonium ions in the aqueous solution. We will denote concentrations in the platinum by [ ]′, and in the aqueous solution by [ ], for instance, $[NH_3]'$ is the concentration of ammonia in the platinum, and $[NH_3]$ the concentration of ammonia in the aqueous solution.

If we have the equilibrium $NH_3 + H \rightleftarrows NH_4$ in the platinum:

$$[NH_4]' = k_2[H]'.[NH_3]' \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* During the course of this investigation, Brönsted (*Zeitsch. physikal. Chem.*, 1911, **77**, 129) has published a paper on the free energy of formation of double salts in which he describes the use of a hydrogen electrode in ammonium chloride solutions under a definite partial pressure of ammonia.

The concentration of ammonia, NH_3, in the platinum will be proportional to the partial pressure of ammonia. Or:

$$[NH_3]' = kp_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

Therefore from (2) and (3):

$$[NH_4]' = k_2k_3[H]'.p_{NH_3} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

Now:

$$[H]' = k_4\sqrt{[H_2]'}$$

and

$$[H_2]' = k_5p_{H_2},$$

where p_{H_2} is the partial pressure of hydrogen over the platinum and solution.

Therefore:

$$[H]' = k_4k_5^{\frac{1}{2}}.p_{H_2}^{\frac{1}{2}}.$$

and from (4):

$$[NH_4]' = k_2k_3k_4k_5^{\frac{1}{2}}p_{NH_3}p_{H_2}^{\frac{1}{2}}.$$

Therefore (1) becomes:

$$e = -\frac{RT}{F}\ln\frac{k_1k_2k_3k_4k_5^{\frac{1}{2}}p_{NH_3}p_{H_2},}{[NH_4^{\cdot}]}$$

or at 25° collecting the constants:

$$e = -0{\cdot}059\log\frac{kp_{NH_3}p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

Even if this electrode reaction $NH_4 \longrightarrow NH_4^{\cdot} + \ominus$ does not actually take place, the potential of the electrode will still be that of the reaction:

$$2NH_3 + H_2 \longrightarrow 2NH_4^{\cdot} + 2\ominus.$$

For if it is simply a hydrogen electrode, we have:

$$e = -0{\cdot}059\log\frac{k_6p_{H_2}^{\frac{1}{2}}}{[H^{\cdot}]} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6).$$

But:

$$[H^{\cdot}] = \frac{K_w}{[OH^{\cdot}]}$$

and

$$[OH'].[NH_4'] = k_7[NH_4OH] = k_8[NH_3] = k_9p_{NH_3},$$

therefore:

$$[OH'] = \frac{k_9p_{NH_3}}{[NH_4^{\cdot}]}$$

and

$$[H^{\cdot}] = \frac{K_w.[NH_4^{\cdot}]}{k_9p} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7).$$

From (6) and (7):

$$e = -0{\cdot}059\log\frac{k_6K_wp_{NH_3}p_{H_2}^{\frac{1}{2}}}{k_9[NH_4^{\cdot}]},$$

or collecting the constants:

$$e = -0{\cdot}059 \log \frac{k p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]},$$

which is identical with (6). Therefore, whether the reaction is:

$$NH_4 \longrightarrow NH_4^{\cdot} + \ominus \quad \text{or} \quad H \longrightarrow H^{\cdot} + \ominus,$$

the potential measured is that of the chemical reaction:

$$2NH_3 + H_2 \longrightarrow 2NH_4^{\cdot}.$$

Experimental.

The solution for the cell was made up by weighing out a certain amount of ammonium chloride dissolving in a solution of ammonia of known strength, and making up to 100 c.c. with this solution. The partial pressure of ammonia over such a solution would be approximately that of the partial pressure of the original ammonia solution. By passing a stream of electrolytic gas through the pure ammonia solution and then through the ammonium chloride solution for some hours, the partial pressure over the latter solution was brought to be the same as that over the former. The arrangement was as follows: A gentle stream of electrolytic gas, prepared by the electrolysis of sodium hydroxide solution, was passed through (1) a wash-bottle of the type used by Gauss (*Zeitsch. anorg. Chem.*, 1900, **25**, 236) containing about 200 c.c. of a solution of ammonia of known concentration; (2) a similar wash-bottle containing the same solution; (3) a wash-bottle (ordinary type) containing ammonium chloride solution of the concentration under investigation; (4) the electrode vessel. After sixteen hours the ammonia solution in the first two wash-bottles was renewed, and a stream of hydrogen substituted for the electrolytic gas. The ammonium electrode was connected with a normal calomel electrode, and measurements of the *E.M.F.* made at intervals for several hours. The *E.M.F.* became constant in forty to fifty minutes, and remained quite steady to 0·3 m.v. The hydrogen was prepared by the action of pure dilute sulphuric acid on pure zinc; it was passed through alkaline permanganate solution, and then over red-hot copper gauze. The electrode vessels were of borosilicate glass.* The electrodes were platinised platinum. The electrode vessel and ammonia solutions were kept in a thermostat at 25°.

The potentials were measured by the compensation method, using a calibrated metre bridge and a galvanometer as null instrument. By means of a resistance in series with the bridge, the standard cell was balanced against about 90 cm. of the wire. The standard cadmium cell, which had been tested at the National Physical

* These vessels were made by Mr. Baumbach, of Manchester.

Laboratory, was taken as 1·0183 volts at 20°. The accuracy of measurement when the resistance of the cell was low was 0·1 m.v. Three normal calomel electrodes were made up as described in Ostwald-Luther's "Physico-Chemische Messungen" (1900). Three decinormal calomel electrodes were also made up. The normal calomel electrodes were tested from time to time against the decinormal electrodes, and were always found to give 0·0534 ± 0·0002 v.

The following cells were measured:

TABLE I.

	E observed.
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(2N)$	0·8604 volt
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(N)$	0·8401 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(0·5N)$	0·8205 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(0·05N)$	0·7622 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid N\text{-}NH_4Cl \mid H_2\ NH_3(0·01N)$	0·7198 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·4N\text{-}NH_4Cl \mid H_2\ NH_3(2N)$	0·8848 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·4N\text{-}NH_4Cl \mid H_2\ NH_3(N)$	0·8631 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·4N\text{-}NH_4Cl \mid H_2\ NH_3(0·5N)$	0·8426 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·4N\text{-}NH_4Cl \mid H_2\ NH_3(0·05N)$	0·7847 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·4N\text{-}NH_4Cl \mid H_2\ NH_3(0·01N)$	0·7436 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·08N\text{-}NH_4Cl \mid H_2\ NH_3(0·05N)$	0·828 ,,
$Hg \mid HgCl_2 N\text{-}KCl \mid N\text{-}KCl \mid 0·08N\text{-}NH_4Cl \mid H_2\ NH_3(0·01N)$	0·788 ,,

$NH_3(2N)$ denotes that the partial pressure of ammonia over the solution was equal to that over a twice normal aqueous ammonia solution. The cells with $0·08N\text{-}NH_4Cl$ had so great a resistance that the measurements were only correct to ±0·1 m.v.

The single potentials of the ammonium electrodes can be calculated from the above values by subtracting 0·283, which is the value of the single potential of the normal calomel electrode at 25°, taking the normal hydrogen electrode as zero. These values are given in table II under e.

From equation (5):

$$e = -0·059 \log \frac{k p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

Therefore:

$$e = e_0 - 0·059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

where e_0 is the normal potential of ammonium. It is the potential which a platinised platinum electrode would give in a solution normal in respect to ammonium ions, the partial pressures of ammonia and hydrogen over the solution being each one atmo-

sphere. In table II under e_0 are the values of this quantity calculated in each case by the equation:

$$e_0 = e + 0{\cdot}059 \log \frac{p_{\mathrm{NH_3}} p_{\mathrm{H_2}}^{\frac{1}{2}}}{[\mathrm{NH_4^{\cdot}}]}.$$

Under $f(c)$ are given the values of

$$0{\cdot}059 \log \frac{p_{\mathrm{NH_3}} p_{\mathrm{H_2}}^{\frac{1}{2}}}{[\mathrm{NH_4^{\cdot}}]}.$$

The *E.M.F.* of the liquid potentials has been neglected, as it is in all the cases considered not greater than one millivolt; the migration ratios of ammonium chloride and potassium chloride are both very nearly 0·5.

TABLE II.

		e.	$f(c)$.	$[\mathrm{NH_4^{\cdot}}]$	$p\mathrm{H_2}$ in mm. of Hg.	$p_{\mathrm{NH_3}}$	e_0
NH_3 (2*N*)	H_2 | *N*-NH_4Cl ...	−0·577	0·089	0·8140	710	27·4	−0·488
NH_3 (*N*)	H_2 | *N*-NH_4Cl ...	−0·557	0·071	0·8135	723	13·52	−0·486
NH_3 (0·5*N*)	H_2 | *N*-NH_4Cl ...	−0·537	0·054	0·8127	730	6·71	−0·483
NH_3 (0·05*N*)	H_2 | *N*-NH_4Cl ...	−0·479	−0·005	0·8110	736	0·667	−0·484
NH_3 (0·01*N*)	H_2 | *N*-NH_4Cl ...	−0·437	−0·047	0·8104	736	0·1334	−0·484
NH_3 (2*N*)	H_2 | 0·4NH_4Cl ...	−0·602	0·111	0·3420	710	27·4	−0·491
NH_3 (*N*)	H_2 | 0·4NH_4Cl ...	−0·580	0·094	0·3415	723	13·52	−0·486
NH_3 (0·5*N*)	H_2 | 0·4NH_4Cl ...	−0·560	0·076	0·3408	730	6 71	−0·484
HH_3 (0·05*N*)	H_2 | 0·4NH_4Cl ...	−0·502	0·017	0·3390	736	0·667	−0·485
NH_3 (0·01*N*)	H_2 | 0·4NH_4Cl ...	−0·461	−0·024	0·3384	736	0·1334	−0·485
NH_3 (0·05*N*)	H_2 | 0·08NH_4Cl..	−0·545	0·056	0·0734	746	0·667	−0·489
NH_3 (0·01*N*)	H_2 | 0·08NH_4Cl..	−0·505	0·015	0·0728	736	0·1334	−0·490
					Mean.. ...		−0·486

Under $[\mathrm{NH_4^{\cdot}}]$, $p_{\mathrm{H_2}}$, and $p_{\mathrm{NH_3}}$ are given the values of these quantities used in calculating $f(c)$ and e_0. The values of $[\mathrm{NH_4^{\cdot}}]$ were taken as the sum of the concentrations of the ions derived from the ammonium chloride and from the ammonia, as though each were independent of the other. It would perhaps be more correct in the strong ammonium chloride solutions to assume that the ammonia was quite inappreciably dissociated, since the high concentration of ammonium ions would throw back the dissociation. If we do this, however, it causes a difference of only 0·1 m.v. in the calculated values of $f(c)$. For the degree of dissociation of ammonium chloride at 0·4 and 0·08*N*, the results of Jones and West (*Amer. Chem. J.*, 1905, **34**, 557) were taken, and the value for *N*-ammonium chloride was obtained by extrapolating from their results. For the ionisation of ammonia, the values of Noyes, Kato, and Sosman (*J. Amer. Chem. Soc.*, 1910, **32**, 159) at 18° up to 0·5*N* were taken. The values for *N* and 2*N* were extrapolated from their values. The values of $p_{\mathrm{NH_3}}$ up to *N*-NH_3 were taken from Locke and Forsall

Amer. Chem. J., 1904, **31**, 268), and the value for $2N$ by extrapolating by the formula $p_{NH_3} = 13{\cdot}34N + 0{\cdot}18N^2$, where N is the normality of ammonia in the solution. In calculating the partial pressure of hydrogen, the vapour pressure of water and of the solutions at 25° was taken as 23 mm. The error introduced by this assumption is less than 0·1 m.v. in the case of N-ammonium chloride. These values were not corrected for changes of barometric pressure, or for the pressure in the electrode vessel being slightly greater than that of the atmosphere. Such differences make no appreciable difference in the value of $f(c)$.

Taking the mean of our values of e_0, we have for the potential of the ammonium electrode at 25°:

$$e = -0{\cdot}486 - 0{\cdot}059 \log \frac{p_{NH_3} p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]}.$$

The agreement of the values of e_0 over wide ranges of concentration is better than for any other hydrogen electrode; for instance, compare the results collected by Wilsmore (*Zeitsch. physikal. Chem.*, 1900, **35**, 302). Moreover, the solutions here investigated were weakly alkaline, whilst Allmand (this vol., p. 842) found that the hydrogen electrode was particularly untrustworthy in dilute alkaline (sodium and potassium hydroxide) solutions. This steadiness of the electrode suggests the probability that the electrode reaction is chiefly $NH_4 \longrightarrow NH_4^{\cdot} + \ominus$, and not $H \longrightarrow H^{\cdot} + \ominus$.

Formation of Complexes.—In the above calculations the formula of the ammonium ion has been supposed to be NH_4, but in the presence of excess of free ammonia it is quite feasible to suppose that NH_3 might be added on, and we should get some complexes of the type $(NH_3)_xH^{\cdot}$. v. Braun (Abegg's "Handbuch," **3**, 74) states that it is not improbable that they exist at high concentrations. By the following method we can determine the average value of x in the solution. If there are no complexes, that is, if the only ions are $NH_4^{\cdot}$ or $NH_3H^{\cdot}$, we shall find $x = 1$.

In the aqueous solution there must exist the equilibrium:

$$xNH_3 + H^{\cdot} \rightleftarrows (NH_3)_xH^{\cdot},$$

and therefore:

$$k[H^{\cdot}] = \frac{[(NH_3)_xH^{\cdot}]}{[NH_3]^x}.$$

In two solutions of different concentrations the ratio of the hydrogen ion concentrations:

$$\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = \frac{[(NH_3)_xH^{\cdot}]_1\,[NH_3]_2^x}{[(NH_3)_xH^{\cdot}]_2\,[NH_3]_1^x}.$$

Taking logarithms:

$$\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = \log\frac{[(NH_3)_xH^{\cdot}]_1}{[(NH_3)_xH^{\cdot}]_2} - x\log\frac{[NH_3]_1}{[NH_3]_2} \quad . \quad . \quad . \quad (8).$$

If, however, the two solutions have the same concentration of ammonium chloride, we have:

$$[(NH_3)_xH^{\cdot}]_1 = [(NH_3)_xH^{\cdot}]_2,$$

and from (8):

$$\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = -x\log\frac{p_1}{p_2},$$

where p is the partial pressure of ammonia.

Therefore:

$$x = \frac{\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2}}{\log\frac{p_2}{p_1}}$$

If we measure of $E.M.F.$ of a cell of the type:

$$NH_3(p_1)H_2 \,|\, NH_4Cl \,|\, H_2NH_3(p_2),$$

we can calculate the value of $\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2}$, for the cell consists of two hydrogen electrodes each with hydrogen at the same pressure, but surrounded by solutions of different hydrogen ion concentration; thus:

$$\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = + \frac{e}{0{\cdot}059}.$$

The values of p_1 and p_2 may be determined as above; x may then be calculated.

In table III are given the values of e observed, and the values of x calculated from them. The value of e was not directly measured; each half of the cell was measured against a normal calomel electrode. The observations are given in table I.

TABLE III.

Cell.					e.	x.
NH_3 (2N)	H_2 |	N-NH_4Cl |	H_2	NH_3 (N)	−0·020	1·18
NH_3 (2N)	H_2 |	0·4 N-NH_4Cl |	H_2	NH_3 (N)	−0·022	1·21
NH_3 (N)	H_2 |	N-NH_4Cl |	H_2	NH_3 (0·5N)	−0·020	1·09
NH_3 (N)	H_2 |	0·4 N-NH_4Cl |	H_2	NH_3 (0·5N)	−0·020	1·09
NH_3 (0·5N)	H_2 |	N-NH_4Cl |	H_2	NH_3 (0·05N)	−0·058	0·99
NH_3 (0·5N)	H_2 |	0·4 N-NH_4Cl |	H_2	NH_3 (0·05N)	−0·058	0·99
NH_3 (0·05N)	H_2 |	N-NH_4Cl |	H_2	NH_3 (0·01N)	−0·042	1·03
NH_3 (0·05N)	H_2 |	0·4 N-NH_4Cl |	H_2	NH_3 (0·01N)	−0·041	1·00
NH_3 (0·05N)	H_2 |	0·08 N-NH_4Cl |	H_2	NH_3 (0·01N)	−0·040	0·97

The values of x are almost exactly unity in the more dilute solutions, although there seems to be a slight tendency to form complexes in the more concentrated solutions. It will be noticed that in the above calculation the pressure of hydrogen has been

assumed to be the same over both electrodes in any one cell. The errors introduced by this assumption are of the order of 1 per cent. in the first and second cells, and quite negligible in the other cells.

In solutions containing no ammonium chloride, that is, in solutions of ammonia in pure water, we have $[OH'] = [(NH_3)_xH^{\cdot}]$, since the concentration of $H^{\cdot}$ is negligible compared with the concentration of ammonium ions. Therefore equation (8) becomes:

$$\log\frac{[H^{\cdot}]_1}{[H^{\cdot}]_2} = \log\frac{[OH']_1}{[OH']_2} - x\log\frac{p_1}{p_2}.$$

But $[OH'] = \frac{K_w}{[H^{\cdot}]}$, where K_w is a constant.

Therefore:

$$2\log\frac{[OH']_2}{[OH']_1} = -x\log\frac{p_1}{p_2},$$

and

$$x = 2\,\frac{\log\dfrac{[OH']_1}{[OH']_2}}{\log\dfrac{p_1}{p_2}}.$$

We can calculate some values of x in pure ammonia solutions by this formula from the results of Noyes, Kato, and Sosman on the ionisation of ammonia solutions, and a knowledge of the pressure of ammonia over the solutions. The data are only available up to $0{\cdot}5N$-ammonia. The values obtained are all approximately unity.

Summary.

The potential of the ammonium electrode at 25° has been determined, and has been shown to depend upon the partial pressures of hydrogen and ammonia, and on the concentration of ammonium ions in the following way:

$$e = -0{\cdot}486 - 0{\cdot}059\log\frac{p_{NH_3}p_{H_2}^{\frac{1}{2}}}{[NH_4^{\cdot}]},$$

where $e = e_{electrode} - e_{solution}$, and the potential of the hydrogen electrode in a solution of normal hydrogen ion concentration is taken as zero.

It has been shown that complexes of the form $(NH_3)_xH^{\cdot}$, where x is greater than one, do not exist to any appreciable extent in dilute aqueous ammonia or ammoniacal ammonium chloride solutions, although there is some evidence of their existence at higher concentrations.

Part of the expenses of this research were borne by a grant from the Chemical Society.

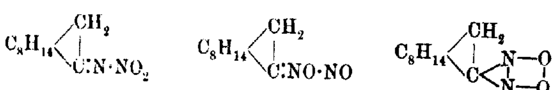
The author wishes to thank Professor F. G. Donnan for his kind interest in this work, and Mr. R. Kingan for some assistance in the experimental work.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTRO-CHEMISTRY,
UNIVERSITY OF LIVERPOOL.

CCXXV.—*Studies in the Camphane Series. Part XXX. Constitution of Pernitrosocamphor (Camphenylnitroamine).*

By MARTIN ONSLOW FORSTER, JOHN ROBERT TROTTER, and JACOB WEINTROUBE.

PERNITROSOCAMPHOR or camphenylnitroamine, discovered by Angeli and Rimini (*Ber.*, 1895, **28**, 1077), and independently by Tiemann (*loc. cit.*, 1079), is produced in association with camphorimine nitrite by the action of nitrous acid on camphoroxime, which also yields the pernitroso-derivative under the influence of dilute nitric acid or of nitrogen peroxide (Trans., 1897, **71**, 197). It has been the subject of numerous inquiries, notably by Hantzsch and Dollfus (*Ber.*, 1902, **35**, 260), Scholl (*Annalen*, 1905, **338**, 1; 1906, **345**, 363), Angelucci (*Annalen*, 1905, **341**, 172), Angeli and Castellana (*Atti R. Accad. Lincei*, 1905, [v], **14**, 669), who directed their efforts principally towards elucidating the problem of atomic arrangement in the N_2O_2-group. Without following the ramifications of this discussion, it may be stated that at present the rival formulæ are:



Hantzsch; Scholl. Angelucci. Angeli and Castellana.

The expression originally used by Tiemann, $C_8H_{14}<\begin{matrix}CH\\ \|\\ C\cdot NH\cdot NO_2\end{matrix}$, in conformity with which he called the substance camphenylnitroamine, no longer meets with favour, although its tautomeric form, $C_8H_{14}<\begin{matrix}CH\\ |\\ C\cdot N:NO\cdot OH\end{matrix}$, is the one used by Hantzsch (*loc. cit.*) in representing the potassium derivative.

In spite of the labour which has been already expended on the problem, it cannot be said that the position is a satisfactory one, and it is difficult to see how a definite conclusion is to be drawn between the nitroimine (Hantzsch and Scholl) and pernitroso-formula (Angeli and Castellana). It is not claimed that the present communication offers a final settlement, but we believe that the fresh material brought forward serves to emphasise an aspect of the question which has hitherto escaped the attention it deserves.

Very soon after the discovery of the substance it was found that the potassium derivative may be readily oxidised to camphoric acid (Mahla and Tiemann, *Ber.*, 1896, **29**, 2811), a fact which confirmed Tiemann in his representation; we find that if potassium ferricyanide is used, camphorquinone is the principal product, which somewhat discounts the presence of an ethenoid linking. Both experiments, however, seem to indicate that in the potassium derivative there exists an association between the pernitroso-group and the second carbon atom (the α-position in camphor) closer than has been hitherto suspected. A more convincing indication of this is to be found in the behaviour of potassium pernitrosocamphor towards diazonium salts. We find that on mixing neutral or slightly alkaline cold aqueous solutions of these materials, there takes place a coupling process, in which the arylazo-group attaches itself to the second carbon atom, leaving the pernitroso-group intact, the products having the properties of camphorquinonearylhydrazones, in which the oxygen is replaced by the pernitroso-group; by the action of hydroxylamine and of semicarbazide on these pernitrosocamphorquinonearylhydrazones, oximes and semicarbazones of the respective camphorquinonearylhydrazones are formed, and in this way there has been obtained, for example, the oxime of camphorquinonephenylhydrazone, previously prepared by the action of hydroxylamine on camphorquinonephenylhydrazone itself (Trans., 1909, **95**, 955):

$$C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}N_2O_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}N_2O_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C{:}N\cdot NH\cdot C_6H_5\\ |\\ C{:}NOH\end{matrix}$$

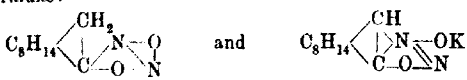
Furthermore, by the action of nitrosyl chloride on potassium pernitrosocamphor, there arises the pernitroso-derivative of *iso*nitrosocamphor, which likewise exchanges the pernitroso-nucleus for the oximino-group under the influence of hydroxylamine, leading to the β-dioxime of camphorquinone:

$$C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}N_2O_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ C{:}N_2O_2\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C{:}NOH\\ |\\ C{:}NOH\end{matrix}$$

Thus it appears that the replacement of oxygen in camphor by the pernitroso-group confers on the α-position properties recalling

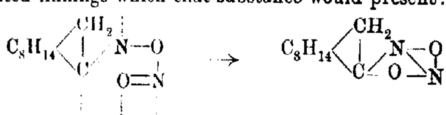
those of the CH_2-group in ethyl malonate, barbituric acid, nitroethane, and kindred substances, with, however, this difference, that pernitrosocamphor does not undergo condensation with benzaldehyde or with *p*-nitrosodimethylaniline.

Although it is not necessary to suppose that in pernitrosocamphor itself there is any direct association between the α-position and the pernitroso-group, it is difficult to believe that the potassium derivative could take part in such changes unless this connexion has been established, and we therefore suggest that the existing knowledge of these substances may be brought into harmony with the formulæ:



Pernitrosocamphor. Potassium derivative.

The above representation of pernitrosocamphor is in agreement with the direct production of the substance from camphoroxime and nitrosyl chloride (Angelucci), and is free from the objection which attaches to regarding the substance as a nitrite of camphoroxime. This latter view is discounted by the following circumstance. If pernitrosocamphor were the nitrite of camphoroxime, alcoholic alkali hydroxide should hydrolyse it to the original oxime, whereas we find that under conditions which leave camphoroxime unchanged, camphor itself is the only product. On the other hand, Angelucci's experiment may be used as an argument in support of the new formula, which might arise from the nitrite of camphoroxime by the mutual satisfaction of the partial valency existing in the two unsaturated linkings which that substance would present:



Camphoroxime nitrite. Pernitrosocamphor.

Moreover, the attachment simultaneously to nitrogen and oxygen, which characterises the carbon atom bearing the pernitroso-group, would in some measure explain the facility with which that group is removed by alkalis, amines, hydroxylamine, and semicarbazide, at the same time accounting for the production of camphoroxime, camphanazine, and the isomeric bornylamines by reducing agents, as observed by Angeli and Castellana.

Whilst it has to be admitted that the suggested formulæ for pernitrosocamphor and its potassium derivative are purely speculative, the same remark applies to those which have been put forward by other workers. They seem to us, however, to offer fewer steric

obstacles to the explanation of the facts. For instance, passage from the labile to the stable form of pernitrosocamphor would be comparatively smooth:

Labile. Stable.

the explanation given by Hantzsch and by Scholl involving a more profound intramolecular disturbance. Moreover, production of the pernitrosocamphorquinonearylhydrazones from the potassium derivative and diazonium salts would harmonise with the mechanism of coupling brought to light by Dimroth and Hartmann (*Ber.*, 1908, **41**, 4012), who showed that when benzenediazonium chloride couples with enolic tribenzoylmethane, a benzene-*O*-azo-compound is formed first, and changes into the isomeric benzene-*C*-azo-compound on fusion. The transference of the benzeneazo-nucleus from oxygen over nitrogen to carbon in enolic pernitrosocamphor is a process more readily conceivable than the alternative explanations, which involve a more circuitous route.

Experimental.

Pernitrosocamphorquinonephenylhydrazone,

$$C_8H_{14}<\begin{matrix}C{:}N{\cdot}NH{\cdot}C_6H_5\\ |\\ C{:}N_2O_2\end{matrix}.$$

A solution of benzenediazonium chloride prepared from 4 grams of aniline was treated at zero with a 20 per cent. solution of sodium carbonate until neutral or faintly alkaline, and then poured into a cold solution of the potassium derivative of pernitrosocamphor (10 grams) in water. The product was a sticky, yellow mass, which was washed by decantation with ice-cold water, and afterwards rubbed with a very small quantity of alcohol, the resulting crystals being drained on porous earthenware; having been treated in this way three or four times, the product was dissolved in cold acetone, from which water precipitated golden-brown crystals. After recrystallisation from warm benzene the compound melted at 104°:

0·1729 gave 28·8 c.c. N_2 at 21° and 745 mm. N = 18·65.

$C_{16}H_{20}O_2N_4$ requires N = 18·66 per cent.

It is noteworthy that on combustion the substance liberates oxygen, which is apt to escape the copper spiral, and indicate a high percentage of nitrogen; the above result, for example, is reduced from over 21 per cent. by absorption with potassium pyrogallate. The substance dissolves readily in organic media, excepting petroleum; a solution containing 0·0997 gram, made up

to 20 c.c. with chloroform, gave α_D 1°52′ in a 1-dcm. tube, whence $[\alpha]_D$ 374·4°. Distinctive colour reactions are given with nitric and sulphuric acids, the latter producing a colour which is intense purple by reflected, deep blue by transmitted light; dilution with water changes this to bright yellow, becoming claret-colour with potassium hydroxide. A solution in concentrated nitric acid is claret-colour by reflected, green by transmitted light, green flocks separating on dilution with water.

Action of Hydroxylamine.—A solution of the pernitroso-derivative in dry pyridine containing excess of free hydroxylamine was allowed to remain during four weeks at 40°, when precipitation with water gave yellow needles, melting at 195°, identical with the oxime of camphorquinonephenylhydrazone already described (*loc. cit.*). The same compound was formed on heating an alcoholic solution of the pernitroso-derivative with aqueous hydroxylamine acetate during two to three hours.

Semicarbazone of Camphorquinonephenylhydrazone,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_5\\ |\\ C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}.$$

The pernitroso-derivative was dissolved in alcohol, and heated with aqueous semicarbazide acetate under reflux during twenty hours; the filtered liquid gave a crystalline residue on evaporation, this being washed with water, and recrystallised from alcohol, which deposited lustrous, golden-yellow, six-sided plates, melting at 268°:

0·1176 gave 24·1 c.c. N_2 at 18° and 746 mm. N = 23·17.

$C_{17}H_{23}ON_5$ requires N = 22·36 per cent.

The semicarbazone dissolves freely in cold acetone, but less readily in hot alcohol; it is sparingly soluble in boiling benzene, and insoluble in hot petroleum. Concentrated nitric acid develops a green coloration.

Pernitrosocamphorquinone-p-nitrophenylhydrazone,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4\cdot NO_2\\ |\\ C:N_2O_2\end{matrix}.$$

On attempting to couple the pernitroso-compound with diazotised *p*-nitroaniline, the product was very sticky, as before, but could not be crystallised. By adding the solution of potassium pernitrosocamphor (10 grams) to the neutralised solution of *p*-nitrobenzenediazonium chloride (prepared from 5·9 grams of *p*-nitroaniline) instead of vice versa, however, the derivative was precipitated in separate particles; after treatment with a small quantity of cold

methyl alcohol, the drained substance was recrystallised from benzene, being deposited in yellow prisms, melting at 96°:

0·1146 gave 18·4 c.c. N_2 at 19° and 747 mm. N = 18·15.

$C_{16}H_{19}O_4N_5$ requires N = 20·29 per cent.

The deficit in nitrogen was shown to be due to solvent of crystallisation, for the substance, after being heated or kept in a desiccator, melted at 178°:

0·9040 lost 0·0959 during five hours at 70°. Loss = 10·61.

0·1470 (residue) gave 26·4 c.c. N_2 at 17° and 764 mm. N = 20·86.

$C_{16}H_{19}O_4N_5 + \frac{1}{2}C_6H_6$ requires loss = 10·16; N = 18·22 per cent.

$C_{16}H_{19}O_4N_5$ requires N = 20·29 per cent.

The substance is readily soluble in acetone and in hot benzene, but is insoluble in petroleum.

*Oxime of Camphorquinone-*p*-nitrophenylhydrazone,*

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4\cdot NO_2 \\ | \\ C:NOH\end{matrix}.$$

On heating an alcoholic solution of pernitrosocamphorquinone-*p*-nitrophenylhydrazone with aqueous hydroxylamine acetate during some hours, the liquid deposited on evaporation a residue which hardened when treated several times with water; recrystallisation from alcohol gave brown needles, melting at 186°:

0·2057 gave 32·3 c.c. N_2 at 18·5° and 755 mm. N = 18·02.

$C_{16}H_{20}O_3N_4$ requires N = 17·72 per cent.

The substance forms a cherry-red solution in concentrated sulphuric acid, whilst alcoholic ammonia develops a brilliant carmine. It dissolves readily in hot alcohol and in cold chloroform or ethyl acetate, but is more sparingly soluble in boiling benzene, and is insoluble in hot petroleum.

*Semicarbazone of Camphorquinone-*p*-nitrophenylhydrazone,*

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4\cdot NO_2 \\ | \\ C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}.$$

This substance was produced on replacing hydroxylamine in the foregoing reaction by semicarbazide; it crystallised from alcohol in golden-yellow plates, melting and decomposing at 250°:

0·1154 gave 23·6 c.c. N_2 at 20° and 755 mm. N = 23·24.

$C_{17}H_{22}O_3N_6$ requires N = 23·45 per cent.

The semicarbazone is freely soluble in cold acetone, but dissolves less readily in chloroform, and only sparingly in boiling benzene; it is insoluble in petroleum. Concentrated sulphuric acid develops an intense, cherry-red coloration, alcoholic ammonia giving a more brownish-red.

Pernitrosocamphorquinone-p-bromophenylhydrazone,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4Br\\ |\\ C:N_2O_2\end{matrix}.$$

This derivative was obtained in two modifications, which differ distinctly from one another in fusibility and specific rotatory power. The product separated in the form of a bright yellow, granular precipitate on adding aqueous potassium pernitrosocamphor to diazotised *p*-bromoaniline rendered alkaline with sodium carbonate; it altered on the filter to a hard, brown cake, which was treated with cold acetone. The undissolved portion was crystallised from benzene by adding petroleum, which precipitated golden-yellow, transparent prisms, melting at 143° with vigorous intumescence:

0·1563 gave 20·5 c.c. N_2 at 17° and 746 mm. N=14·91.
0·2780 ,, 0·1378 AgBr. Br=21·09.
$C_{16}H_{19}O_2N_4Br$ requires N=14·77; Br=21·11 per cent.

A solution containing 0·2941 gram, made up to 25 c.c. with chloroform, gave α_D 7°5′ in a 2-dcm. tube, whence $[\alpha]_D$ 301·0°, this value remaining unaltered during ten days. The substance develops an intense, chocolate-brown coloration with concentrated sulphuric acid, changing to weak claret colour, with faint green dichroism, on adding nitric acid.

The acetone filtrate from the foregoing substance deposited a dark brown oil on evaporation, this becoming solid when stirred with dilute hydrochloric acid; recrystallisation from benzene to which petroleum was added gave clear-cut, yellow, transparent prisms, melting at 159°:

0·1823 gave 24·4 c.c. N_2 at 19° and 737 mm. N=14·91.
0·3326 ,, 0·1642 AgBr. Br=21·01.
$C_{16}H_{19}O_2N_4Br$ requires N=14·77; Br=21·11 per cent.

A solution containing 0·2335 gram, made up to 25 c.c. with chloroform, gave α_D 5°50′ in a 2-dcm. tube when examined immediately; in the course of ten days this had fallen to 4°24′, when the liquid was almost too dark to transmit the necessary light. The initial and final readings correspond with $[\alpha]_D$ 312·3° and 235·5° respectively. In recrystallising the substance from a mixture of benzene and petroleum, it was noticed that nodules separated first, followed by silky, yellow needles; no other difference could be detected between these two forms, and on one occasion when a mixture of nodules and needles had separated, the former changed into the latter during one night in the mother liquor.

The dichroism of the bromo-derivative of higher melting point in sulphuric-nitric acid is distinct from that of the more fusible

one, the secondary colour being bright blue. The principal difference between the two substances, however, lies in the behaviour towards petroleum (b. p. 60—80°); this does not dissolve the derivative of higher melting point, whilst 1 gram of the isomeride requires less than 100 c.c. of the boiling solvent for dissolution, separating in lustrous, six-sided plates.

Oxime of Camphorquinone-p-*bromophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4Br\\ |\\ C:NOH\end{matrix}.$$

This substance, prepared from the higher melting bromophenylhydrazone and hydroxylamine acetate in aqueous alcohol, crystallised from alcohol in rectangular, primrose prisms, melting at 180°:

0·1989 gave 21·8 c.c. N_2 at 19° and 738 mm. N = 12·25.

$C_{16}H_{20}ON_3Br$ requires N = 12·00 per cent.

A solution containing 0·1950 gram, made up to 20 c.c. with chloroform, gave α_D 4°13′ in the 2-dcm. tube, whence $[\alpha]_D$ 215·5°. An intense, red coloration is developed by concentrated sulphuric acid, and is bleached on adding nitric acid. The oxime is very sparingly soluble in boiling petroleum, but dissolves freely in cold acetone, chloroform, methyl alcohol, ethyl acetate, or boiling benzene.

Semicarbazone of Camphorquinone-p-*bromophenylhydrazone*,

$$C_8H_{14}<\begin{matrix}C:N\cdot NH\cdot C_6H_4Br\\ |\\ C:N\cdot NH\cdot CO\cdot NH_2\end{matrix}.$$

This was also prepared from the less fusible bromophenylhydrazone, and crystallised from alcohol in brown, six-sided plates, melting at 265°:

0·1481 gave 22·7 c.c. N_2 at 18° and 760 mm. N = 17·70.

$C_{17}H_{22}ON_5Br$ requires N = 17·85 per cent.

The substance is insoluble in petroleum, and dissolves only sparingly in boiling benzene; it is moderately soluble in hot methyl alcohol.

Pernitrosocamphorquinoneoxime (*Pernitroso*iso*nitrosocamphor*),

$$C_8H_{14}<\begin{matrix}C:NOH\\ |\\ C:N_2O_2\end{matrix}.$$

Preliminary experiments showed that there is not any action between potassium pernitrosocamphor and amyl nitrite, even in presence of sodium ethoxide, but nitrosyl chloride, although regenerating a considerable proportion of pernitrosocamphor, leads also to the *iso*nitroso-compound.

Ten grams of the potassium derivative suspended in dry ether were subjected to the action of nitrosyl chloride gas until the liquid became yellow, when it was shaken with dilute sodium hydroxide, and left about 5 grams of pernitrosocamphor on evaporation; the alkaline solution was bright yellow, and gave a bulky, colourless precipitate with hydrochloric acid, amounting, in various experiments, to between 1 and 3 grams. Recrystallisation from dilute alcohol gave colourless needles, petroleum depositing indefinite, fern-like crystals, resembling those of *iso*nitrosocamphor, and melting at 147.5°:

0·1418 gave 23·5 c.c. N_2 at 17° and 750 mm. N = 18·96.

$C_{10}H_{15}O_3N_3$ requires N = 18·66 per cent.

A solution containing 0·1415 gram, made up to 25 c.c. with chloroform, gave α_D 1°10′ in the 2-dcm. tube, whence $[\alpha]_D$ 103·1°. The substance is freely soluble in organic media, excepting petroleum, 250 c.c. of which (b. p. 80—100°) were required by 1·5 gram; it dissolves immediately in sodium hydroxide, developing a yellow coloration, and on adding freshly prepared ferrous sulphate solution to the diluted liquid there is a greenish-blue precipitate, rapidly becoming dark brown, quite distinct from the purple substance produced by *iso*nitrosocamphor in similar circumstances. On allowing an alcoholic solution to remain at 40° with excess of hydroxylamine acetate in water, camphorquinone-β-dioxime began to crystallise within two hours.

The *benzoyl* derivative, $C_8H_{14}<\begin{matrix}C{:}NO{\cdot}CO{\cdot}C_6H_5\\ |\\ C{:}N_2O_2\end{matrix}$, prepared from the sodium derivative and benzoyl chloride, dissolved with unexpected difficulty in hot alcohol, from which it crystallises in lustrous, transparent, six-sided prisms, becoming yellow and decomposing at 174°:

0·1792 gave 20·3 c.c. N_2 at 18° and 748 mm. N = 12·87.

$C_{17}H_{19}O_4N_3$ requires N = 12·62 per cent.

A solution containing 0·1491 gram, made up to 25 c.c. with chloroform, gave α_D 1°31′ in a 3-dcm. tube, whence $[\alpha]_D$ 84·7°. The substance is readily soluble in chloroform, acetone, ethyl acetate, and warm benzene, sparingly so in boiling petroleum; on adding 20 per cent. sodium hydroxide to the boiling alcoholic solution there is developed the deep yellow coloration of the sodium derivative, showing that the rearrangement leading to the colourless benzoyl derivative of *iso*nitrosocamphor does not occur on benzoylating the pernitroso-compound.

Production of Camphor from Pernitrosocamphor.

Tiemann showed that hydriodic acid removes the pernitroso-group and regenerates camphor (*Ber.*, 1895, **28**, 1081), which was recognised also by Angeli and Castellana (*loc. cit.*) in the complex mixture of materials arising from the pernitroso-derivative by reduction; this includes the two isomeric bornylamines, camphoroxime, camphene, camphanazine, nitrous acid, and nitrogen. We find that whilst hydrogen sulphide is without action on pernitrosocamphor in alcoholic solution, addition of ammonia causes the liquid to turn red and evolve gas; evaporation of the alcohol leaves camphor, which is also regenerated easily and quantitatively from the pernitroso-derivative by the action of alcoholic sodium hydroxide. Three grams in 10 grams of alcohol were heated with 2 grams of sodium hydroxide in 8 grams of water during three hours under reflux, when distillation in steam gave the expected quantity of camphor; a control experiment in which camphoroxime was substituted for pernitrosocamphor showed that under the above conditions the oxime undergoes no change. Hence the production of camphor by hydrolysis cannot depend on intermediate formation of camphoroxime.

Aniline also may be used for the recovery of camphor from the pernitroso-derivative, doubtless owing to the production of phenyliminocamphane, $C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}N{\cdot}C_6H_5\end{matrix}$, which might be expected to undergo hydrolysis with great facility. When alcoholic solutions are heated, gas is liberated, and after a short interval the liquid gives camphor with hydrochloric acid; another experiment, in which the two materials were left in contact during many months at laboratory temperature, gave crystals of camphor without addition of acid, suggesting that phenyliminocamphane must be a highly unstable substance.

Action of Hydrazine on Pernitrosocamphor.

Angeli and Castellana have shown (*loc. cit.*) that the action of hydrazine on pernitrosocamphor leads to camphanazine, and this we find to be the case if the materials are heated together; the following experiment, however, seems to indicate that this is a secondary product, arising from decomposition of the unstable camphorhydrazone, $C_8H_{14}<\begin{matrix}CH_2\\ |\\ C{:}N{\cdot}NH_2\end{matrix}$, recently isolated by Kijner (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 582). Five grams of potassium pernitrosocamphor were covered with hydrazine hydrate

(60 per cent.), and allowed to remain in a stoppered vessel. At first there was not any noticeable change, but gradually the pasty mass became inflated with gas, and in the course of several weeks the crystals disappeared, leaving a viscous oil floating on the liquid. After two months this was extracted with ether, washed with water until the latter was without action on Fehling's solution, and then recovered by evaporating the ether without heat; the viscous residue had an odour resembling that of bornylamine, and reduced ammoniacal silver oxide when heated, whilst oxidation with hot aqueous mercury acetamide led to camphor. The remainder was therefore shaken with benzoyl chloride in 10 per cent. sodium hydroxide, giving rise to camphor benzoylhydrazone (see below), indicating that camphorhydrazone had been produced by the action of hydrazine hydrate on pernitrosocamphor.

Camphor Benzoylhydrazone, $C_8H_{14}<\begin{matrix}CH_2\\ | \\ C:N\cdot NH\cdot CO\cdot C_6H_5\end{matrix}$.

On allowing molecular proportions of pernitrosocamphor and benzoylhydrazine to remain a few days in aqueous alcohol, lustrous, silky needles separated, melting at 171° after recrystallisation from methyl alcohol:

0·2006 gave 18·2 c.c. N_2 at 22° and 768 mm. N = 10·39.

$C_{17}H_{22}ON_2$ requires N = 10·37 per cent.

A solution containing 0·3791 gram, made up to 25 c.c. with chloroform, gave α_D $-1°32'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-50·5°$. Whilst freely soluble in cold acetone and chloroform, benzene, alcohol, and ethyl acetate dissolve only moderate proportions, and it is sparingly soluble in boiling petroleum. Concentrated sulphuric acid hydrolyses the substance to camphor, hydrazine, and benzoic acid.

ROYAL COLLEGE OF SCIENCE, LONDON.
SOUTH KENSINGTON, S.W.

CCXXVI.—*The Constituents of the Seeds of* Casimiroa edulis.

By Frederick Belding Power and Thomas Callan.

The *Casimiroa edulis*, La Llave and Lejarza (Nat. Ord. *Rutaceae*), is a tree which is widely distributed throughout Mexico and Central America. It is known in Mexico by the vernacular names of "Chochitzapotl" and "Iztactzapotl," and in Guatemala as "Mato sano." Under the title of "Zapote blanco," the Pharmacopœia of Mexico recognises the fruit and the seed of the *Casimiroa*, indicating the former to be used as an anthelmintic and the latter as a vulnerary, for which purpose the kernels of the seed are roasted and powdered. The fruit, as the specific name of the plant denotes, is edible, and has an agreeable flavour, although it is stated to induce sleep, whereas it has been recorded that the kernels of the seed are deleterious or even fatal in their effects (Hernandez, *Rerum medicarum Novae Hispaniae thesaurus*, etc., *Romae*, 1651, *Lib.* III., p. 89).

The first chemical investigation of the seed of the *Casimiroa* was by José Sanchez, who, in a thesis published in Mexico in 1893, indicated the presence of a crystalline substance giving the general reactions of an alkaloid, together with two resins, an essential oil, fatty matter, gum, glucose, and starch. The alkaloidal substance was considered to be the probable source of the reputed physiological action of the seed. In 1898 a Commission was appointed in Mexico for the botanical and chemical study of the *Casimiroa*, and for the purpose of determining its therapeutic value. As a result of this inquiry, it was stated by Altamirano that the seed contains a glucoside, which, however, could be obtained only as a pale yellow, amorphous mass. This product, which he regarded as the active principle, possessed a taste which was at first sweet, but afterwards bitter and persistent. It was soluble in water and in alcohol, and its solution yielded precipitates with the usual alkaloid reagents. The results of a subsequent study by Bocquillon, in France, were incorporated in a thesis entitled, "Étude botanique et pharmacologique des Xanthoxyléas-Casimiroa," 1901, pp. 104, and more recently the subject has been investigated by Bickern (*Arch. Pharm.*, 1903, **241**, 166). A series of pharmacological investigations relating to the *Casimiroa* has furthermore been recorded by Robin and Coyon, by Chevalier, and by Vincent in *Bull. gén. de thérapeutique*, 1909, **158**, 16, 96, 193, 241, the last-mentioned author having also given a complete historical survey of the subject.

The chemical examination of *Casimiroa* seeds by Bickern (*loc. cit.*) was apparently conducted with a very small quantity of material, the amount not being directly stated; but from the results obtained he was led to conclude that they contain a "glucoalkaloid," melting at 106°, to which he assigned the name "casimirin," and the formula $C_{30}H_{32}O_5N_2$. This formula, however, was based on but one analysis, and its theoretical percentage figures were incorrectly recorded. Nevertheless, the substance was stated to undergo hydrolysis by heating with 30 per cent. hydrochloric acid, with the formation of an alkaloid, $C_{54}H_{54}O_5N_4$, and dextrose, in accordance with the equation:

$$2C_{30}H_{32}O_5N_2 + H_2O = C_{54}H_{54}O_5N_4 + C_6H_{12}O_6.$$

In this case also a considerable discrepancy in the figures appears to exist, inasmuch as an analysis of the residual alkaloid indicated it to contain 73·2 per cent. of carbon, whereas the formula $C_{54}H_{54}O_5N_4$ requires C=77·3 per cent. It would, moreover, be impossible for a substance of the composition $C_{30}H_{32}O_5N_2$ to yield dextrose on hydrolysis, inasmuch as it contains but five oxygen atoms.

Another compound described by Bickern (*loc. cit.*) was obtained by mixing the powdered seed with lime, and extracting with ether, when, on evaporating the solvent, a colourless substance was precipitated. The latter, when crystallised from chloroform, separated in colourless needles, melting at 207°, and to it the name "casimirol" and the formula $C_{27}H_{48}O_2$ were assigned. As this substance yielded colour reactions similar to those of the phytosterols, it was assumed to be related to that class of compounds.

It was furthermore noted by Bickern that the above-mentioned substances, as well as various ethereal and alcoholic extracts of the seed, were tested on animals by Professor Cloëtta, of Zurich, but were found to be devoid of any hypnotic action. On the other hand, Chevalier (*loc. cit.*, p. 96) was led to conclude from the results of his experiments on animals that the therapeutic value of *Casimiroa* seed is due to the essential oil and resin they contain (compare also *Lancet*, August 21st, 1909, p. 561).

From the preceding brief review of the literature it will be observed that the statements respecting the constituents and physiological action of *Casimiroa* seeds are very divergent, and, to a large extent, inconclusive. In view of the interest pertaining to the subject it was deemed desirable to submit these seed to a more complete examination, and the results are embodied in the present communication.

Experimental.

Inasmuch as the entire fruit of *Casimiroa edulis* could not conveniently be transported to this country, and the seed are considered to be the most active portion, a quantity of the latter was specially collected in Mexico for the purpose of the present investigation. The seed, which in size and shape somewhat resemble an almond, are provided with a grey, fibrous shell, enclosing a kernel, which is covered with a thin, brown membrane. The shells were found to represent about one-fifth the weight of the entire fresh seed, and they were separately examined.

I.—*Examination of the Kernels.*

Separation of an Enzyme.

A quantity (810 grams) of the kernels, representing 1 kilogram of the entire seed, was crushed, and macerated with water at the ordinary temperature for two days, the liquid being then expressed and filtered. To the filtered liquid, in which the presence of starch was indicated, about twice its volume of alcohol was added, when an abundant flocculent precipitate was produced. After about twenty-four hours the precipitate was collected, washed with a little alcohol, and dried, first on a porous plate, and finally in a vacuum over sulphuric acid. It could then be reduced to a light brown powder, and amounted to 9 grams, or 0·9 per cent. of the weight of entire seed employed.

The above-described product, when dissolved in water, yielded a solution which frothed strongly on agitation, and gave an abundant, white, curdy precipitate, both with hydrochloric acid and on boiling. It gave the biuret reaction, and also slowly hydrolysed amygdalin, thus proving the presence of an enzyme.

Preliminary Test for an Alkaloid.—A small portion (about 6 grams) of the dried kernels of the seed was treated with Prollius' fluid, and the resulting liquid tested in the usual manner for an alkaloid. The results obtained indicated the presence of a considerable proportion of such a substance.

For the purpose of a complete examination of the seed, the shells were first separated from the kernels, and a quantity of the latter, which, after being ground, amounted to 37·05 kilograms, was extracted by continuous percolation with hot alcohol until exhausted. In view of the asserted presence of a glucoside, or of a "glucoalkaloid," in the seed, and in order to preclude the hydro-

lysis of such a substance, all the preliminary operations were conducted as quickly as possible. After the removal of the greater portion of the alcohol, the amount of thin extract obtained was 11·45 kilograms.

Distillation of the Extract with Steam. Separation of an Essential Oil.

The entire amount of extract was subjected to distillation in a current of steam, and the distillate, which contained some oily drops in suspension, extracted with ether. After the removal of the solvent, a quantity (8 grams) of an oily liquid was obtained, which, when distilled under diminished pressure, passed over between 80° and 160°/25 mm., but for the most part below 130°/25 mm. This essential oil, when freshly distilled, had a pale yellow colour, but gradually darkened on keeping, even in absence of air. It possessed an agreeable, aromatic odour, and the following constants: $d = 0{\cdot}9574$ at 20°; α_D $-2°25'$ in a 25 mm. tube. It gave no coloration with ferric chloride, and did not respond to the test for furfuraldehyde.

Non-volatile Constituents of the Extract.

After the above-described operation, there remained in the distillation vessel a dark-coloured aqueous liquid (A), together with a quantity of a soft, oily resin (B). These products were separated, and the resin thoroughly washed with hot water, the washings being added to the main portion of the aqueous liquid.

Examination of the Aqueous Liquid (A).

The aqueous liquid was repeatedly extracted with large quantities of ether, and the ethereal liquid, after concentrating to a convenient bulk, was shaken successively with aqueous ammonium carbonate, sodium carbonate, and sodium hydroxide.

Isolation of a New Alkaloid, Casimiroine, $C_{24}H_{20}O_8N_2$.

On shaking the ethereal extract of the aqueous liquid with a concentrated solution of ammonium carbonate, a crystalline substance slowly separated, and remained suspended in the alkaline liquid. This substance was collected, and amounted to 2·8 grams. It crystallised very readily from alcohol or ethyl acetate, separating in rosettes of colourless needles, and melted at 196—197°. Although very sparingly soluble in water, its aqueous solution, when acidified, gave copious precipitates with the usual alkaloidal reagents, such

as solutions of iodine in potassium iodide, potassium-mercuric iodide, and picric acid:

0·1170 gave 0·2670 CO_2 and 0·0514 H_2O. C = 62·2; H = 4·9.

0·1322 „ 7·2 c.c. N_2 at 16° and 768 mm. N = 6·4.

$C_{24}H_{20}O_8N_2$ requires C = 62·1; H = 4·3; N = 6·0 per cent.

These results, together with a subsequent analysis of its aurichloride, indicate the above-described alkaloid to possess the formula $C_{24}H_{20}O_8N_2$, and, being a new compound, it is proposed to designate it *casimiroine*.

Casimiroine contains two methoxyl groups, as the following determination by Perkins's modification of the Zeisel method has shown:

0·2790 gave 0·2886 AgI. MeO = 13·6.

$C_{22}H_{14}O_6N_2(OMe)_2$ requires MeO = 13·4 per cent.

Casimiroine is a very weak base, since it is precipitated from its solution in concentrated hydrochloric acid by dilution with water. The only crystalline salts that could be obtained were the *picrate* and the *aurichloride*. The picrate, which was very sparingly soluble, crystallised in small, yellow needles, melting at 165°.

Casimiroine Aurichloride, $C_{24}H_{20}O_8N_2,HAuCl_4$.—This salt was prepared by adding a solution of gold chloride to a dilute solution of casimiroine in aqueous alcohol containing a little hydrochloric acid. The yellow precipitate thus produced was crystallised from alcohol, when the salt was obtained in handsome, orange-yellow needles, melting at 195—196°:

0·1508 gave 0·1998 CO_2 and 0·0460 H_2O. C = 36·1; H = 3·4.

0·1207 „ , on ignition, 0·0296 Au. Au = 24·5.

$C_{24}H_{20}O_8N_2,HAuCl_4$ requires C = 35·8; H = 2·6; Au = 24·5 per cent.

A solution of the alkaloid in chloroform was found to be devoid of optical activity.

When a little casimiroine, on a porcelain tile, is moistened with a drop of concentrated nitric acid, a yellow colour is first produced, which rapidly deepens to orange-red. With concentrated sulphuric acid the alkaloid, when similarly treated, develops a pale green colour, which, on the addition of a trace of nitric acid, immediately changes to a brilliant orange hue.

Hydrolysis of Casimiroine.

Formation of a New Base, Casimiroitine, $C_{23}H_{22}O_7N_2$.

On boiling casimiroine for several hours with an alcoholic solution of potassium hydroxide, and then adding a small quantity of water, long, glistening, hair-like needles separate from the liquid

on cooling. By the careful fractional crystallisation of this product from ethyl acetate it was observed not to be homogeneous but to consist mainly of a substance which separated in stout prisms, melting at 171°, together with a small quantity of a substance which crystallised in fan-like tufts of slender needles, melting at 159°. Only the first-mentioned substance (m. p. 171°) was obtained in an amount sufficient for analysis. On recrystallising this from dilute alcohol, it was obtained, like the original product, in long, glistening, hair-like needles, which formed a felty mass, greatly resembling glass-wool:

0·2680, dried at 110° to a constant weight, lost 0·0188 H_2O. $H_2O = 7·0$.

0·1106 * gave 0·2561 CO_2 and 0·0540 H_2O. C = 63·1; H = 5·4.

0·1560 * „ 8·6 c.c. N_2 at 12·5° and 774 mm. N = 6·6.

$C_{23}H_{22}O_7N_2$ requires C = 63·0; H = 5·0; N = 6·4 per cent.

$C_{23}H_{22}O_7N_2,2H_2O$ requires $H_2O = 7·6$ per cent.

The above-described hydrolytic product is thus shown to possess the formula $C_{23}H_{22}O_7N_2$, and, being a new compound, it may be designated *casimiroitine*. It appears to have been formed from casimiroine by the addition of a molecule of water and the elimination of a molecule of carbon dioxide, according to the following equation:

$$C_{24}H_{20}O_8N_2 + H_2O = C_{23}H_{22}O_7N_2 + CO_2.$$

When casimiroine is boiled for a few minutes with concentrated hydrochloric acid, it yields an acid which is very sparingly soluble in alcohol and water, and melts above 300°. The amount of material available did not permit of the further study of this reaction.

Isolation of Benzoic Acid.

The ammonium carbonate solution, from which the suspended alkaloid, casimiroine, had been removed by filtration, as already described, was acidified, when a quantity of dark, resinous material was precipitated. As nothing crystalline could be directly isolated from this product, it was dissolved in methyl alcohol, and dry hydrogen chloride passed into the hot solution. The esterified mixture was then poured into water and extracted with ether, the ethereal liquid being subsequently shaken with a dilute solution of sodium hydroxide. The non-phenolic portion of the product possessed the odour of methyl benzoate, and on hydrolysis yielded a small amount of an acid (m. p. 120°), which was identified as benzoic acid. The phenolic portion contained a substance which

* Anhydrous substance.

ive an intense violet coloration with ferric chloride, and was idently salicylic acid, but the amount of the latter was too small permit of its isolation.

The original ethereal extract of the aqueous liquid, which had en shaken with a solution of ammonium carbonate, as previously scribed, was subsequently extracted successively with aqueous dium carbonate and sodium hydroxide. These alkalis, however, moved only dark-coloured, resinous material, and on finally aporating the ethereal liquid it left but a slight, oily residue.

Isolation of a New Alkaloid, Casimiroedine, $C_{17}H_{24}O_5N_2$.

The original aqueous liquid, which had been completely extracted ith ether, was next shaken repeatedly with hot amyl alcohol. A ortion of the amyl-alcoholic extract was concentrated under iminished pressure to a small bulk, when, on cooling, a quantity f dark-coloured, solid material separated. On treating this with small amount of cold alcohol, most of the colouring matter was emoved, leaving a slightly coloured, apparently crystalline sub- stance. After the separation of the latter, no other crystalline substance could be isolated from the dark-coloured material, even after heating it with 5 per cent. sulphuric acid. As the above-mentioned substance was readily soluble in dilute acids, its isolation was found to be most easily effected by shaking the amyl-alcoholic extract with aqueous 2 per cent. sulphuric acid until the acid liquid ceased to give a precipitate with an aqueous solution of iodine in potassium iodide, and the larger remaining portion of the extract was therefore treated in this manner. The sulphuric acid was subsequently removed from the aqueous liquid by means of barium hydroxide, and the excess of the latter by carbon dioxide, after which the liquid was filtered and concentrated. During the process of evaporation the substance separated in the form of crusts, and the total amount so obtained was 16 grams. The substance, which was found to contain nitrogen, was recrystallised from alcohol, when it separated in wart-like aggregates of very small needles, melting at 222—223°:

0·1613 gave 0·3587 CO_2 and 0·0980 H_2O. C = 60·6; H = 6·8.

0·1466 „ 10·8 c.c. N_2 at 11° and 743 mm. N = 8·6.

$C_{17}H_{24}O_5N_2$ requires C = 60·7; H = 7·1; N = 8·3 per cent.

The above-described substance, which has thus been shown to be an alkaloid, evidently possesses the formula $C_{17}H_{24}O_5N_2$. As it is a new compound, it is proposed to designate it *casimiroedine*.

Casimiroedine is a fairly strong base, since it dissolves readily

in dilute acids, and on rendering the solution alkaline the alkaloid only slowly separates in the form of rosettes of needles. It is very sparingly soluble in chloroform, ether, benzene, ethyl acetate, or cold alcohol, but is readily soluble in hot alcohol, and amyl alcohol dissolves it freely.

A slightly acidified solution of casimiroedine, even when exceedingly dilute, gives a reddish-brown precipitate with a solution of iodine in potassium iodide, but potassium-mercuric iodide and picric acid only yield precipitates with a somewhat concentrated solution.

The alkaloid in acid solution was found to be optically active, and a determination of its rotatory power gave the following result:

0·4198, made up to 20 c.c. with 1 per cent. hydrochloric acid, gave α_D $-1°32'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-36·5°$.

Casimiroedine was found to contain no methoxyl group, and in its chemical behaviour is a very indifferent substance. No crystalline derivative could be prepared from it with the exception of the *aurichloride*.

Casimiroedine Aurichloride, $C_{17}H_{24}O_5N_2,HAuCl_4,2H_2O$.—On the addition of a concentrated solution of gold chloride to a fairly strong solution of casimiroedine in hydrochloric acid the aurichloride is precipitated as an oil, which crystallises on stirring. This salt is dissociated in contact with water, but could be crystallised from 20 per cent. aqueous hydrochloric acid, when it separated in bright yellow, microscopic needles, which melt indefinitely at about 90° in their water of crystallisation. After drying at 70°, however, the salt melts and completely decomposes at 145—148°:

0·0984, dried at 100° to a constant weight, lost 0·0054 H_2O. $H_2O = 5·5$.

0·0930 (dried salt) gave, on ignition, 0·0272 Au. Au = 29·2.

$C_{17}H_{24}O_5N_2,HAuCl_4,2H_2O$ requires $H_2O = 5·1$ per cent.

$C_{17}H_{24}O_5N_2,HAuCl_4$ requires Au = 29·2 per cent.

The original aqueous liquid, which had been completely extracted with both ether and amyl alcohol, as already described, was subsequently treated with a slight excess of solution of basic lead acetate. A voluminous, light brown precipitate was thus produced, which was collected, thoroughly washed, and decomposed with hydrogen sulphide, but it yielded nothing definite. The filtrate from the basic lead acetate precipitate was treated with hydrogen sulphide for the removal of the excess of lead, and the filtered liquid concentrated under diminished pressure. It then formed a viscid syrup, which contained a considerable quantity of sugar,

since it readily yielded *d*-phenylglucosazone, melting at 205—207°. A portion of the syrup was heated for two hours with dilute sulphuric acid in a reflux apparatus, and then distilled in a current of steam. The distillate contained traces of formic and acetic acids, and on extracting the liquid remaining in the distillation flask with ether, only a further small amount of these acids was obtained. The aqueous liquid was finally treated with barium hydroxide for the removal of the sulphuric acid, filtered, and concentrated, but no crystalline product separated, even after keeping for a considerable time. There was therefore no evidence that the original aqueous liquid contained any substance of a glucosidic nature.

Examination of the Resin (B).

The resinous material, representing that portion of the alcoholic extract of the kernels of the seed which was insoluble in water, formed a soft, oily mass, and amounted to about 375 grams. It was dissolved in alcohol, mixed with purified sawdust, and the thoroughly dried mixture extracted successively in a Soxhlet apparatus with light petroleum (b. p. 35—50°), ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This extract, after the complete removal of the solvent, was a thin, dark-coloured, oily product, amounting to 256 grams. It was digested with 1 litre of ether, when 3·2 grams of a white, apparently crystalline substance remained undissolved, and were collected. This was resolved by fractional crystallisation from alcohol into a substance which was obtained in the form of needles, melting at 196—197°, and amounting to 1·5 grams, and a substance which melted at 232—233°. The first-mentioned substance consisted of the previously described alkaloid, casimiroine, which had been isolated from the aqueous liquid, whilst the second substance was subsequently obtained in much larger amount from the ethereal extract of the resin, and will be further considered in connexion with the latter.

After the separation of the above-mentioned crystalline substances, the clear ethereal solution of the petroleum extract was shaken with aqueous ammonium carbonate, which, however, removed only traces of resinous material. On subsequently attempting to extract the ethereal liquid with sodium carbonate and sodium hydroxide, intractable emulsions were formed. The ether was therefore removed, and the residue hydrolysed by heating with a

solution of 90 grams of potassium hydroxide in one litre of alcohol. After the removal of the alcohol, water was added, and the alkaline liquid repeatedly extracted with ether.

Isolation of Sitosterol, $C_{27}H_{46}O,H_2O$.

The ethereal extract of the alkaline liquid was dried, and the solvent evaporated. A pale yellow, crystalline product was thus obtained, which was dissolved in hot alcohol, when, on cooling, a quantity (8·8 grams) of a substance separated in colourless plates. On recrystallising the substance from a mixture of ethyl acetate and dilute alcohol, it was obtained in needles, melting at 134—135°:

0·2263, on heating at 100°, lost 0·0114 H_2O. $H_2O = 5·0$.
0·1048 * gave 0·3218 CO_2 and 0·1153 H_2O. C = 83·7; H = 12·2.
$C_{27}H_{46}O,H_2O$ requires $H_2O = 4·5$ per cent.
$C_{27}H_{46}O$ requires C = 83·9; H = 11·9 per cent.

The substance was thus identified as a phytosterol, and it gave the colour reactions of that class of compounds.

A determination of its optical rotatory power gave the following result:

0·3118,* made up to 20 c.c. with chloroform, gave α_D −1°0′ in a 2-dcm. tube, whence $[\alpha]_D$ −32·1°.

The phytosterol gave an acetyl derivative, which separated from acetic anhydride in small needles, melting at 126—127°. Its identity with sitosterol was therefore established.

The original alcoholic mother liquor remaining from the crystallisation of the sitosterol was evaporated, when a quantity (10 grams) of viscid, oily material was obtained. This was found to consist chiefly of oxygenated substances, but nothing definite could be isolated from it.

Isolation of Ipuranol, $C_{23}H_{38}O_2(OH)_2$.

The alkaline liquid, from which the sitosterol had been removed by extraction with ether, was acidified, and the liberated fatty acids taken up with ether. The ethereal liquid contained a quantity of a dark-coloured, crystalline substance in suspension. This was collected, heated with alcohol for the removal of colouring matter, and then recrystallised from dilute pyridine, from which it separated in microscopic needles, melting at 280—285°. The amount of substance so obtained was 2·9 grams. (Found, C = 72·6; H = 10·4. Calc., C = 72·6; H = 10·5 per cent.)

* Anhydrous substance.

The above results, together with the colour reactions yielded by this substance, established its identity as ipuranol.

When heated with acetic anhydride it gave diacetylipuranol, which separated from alcohol in shining leaflets, melting at 166°. (Found, C = 69·7; H = 9·5. Calc., C = 69·8; H = 9·5 per cent.)

On heating the ipuranol, in pyridine solution, with benzoyl chloride, a *dibenzoyl* derivative was obtained, which, after crystallisation from a mixture of ethyl acetate and alcohol, separated in needles melting at 197°.

A determination of the optical rotatory power of the ipuranol gave the following result:

0·1708, made up to 20 c.c. with pyridine, gave α_D −0°41′ in a 2-dcm. tube, whence $[\alpha]_D$ −40·0°.

Identification of the Fatty Acids.

The ethereal liquid from which the ipuranol had been removed, as above described, was evaporated to a low bulk, and a large quantity of light petroleum added. This precipitated some resinous material, which was separated, after which the liquid was again evaporated. A quantity (105 grams) of fatty acids was thus obtained, which, when distilled under diminished pressure, passed over between 200° and 230°/12 mm.

In order to effect a separation of the solid and liquid acids, a portion (25 grams) of the mixture was converted into the lead salts, and the latter digested with ether, when the greater part dissolved. Both the soluble and insoluble portions were decomposed by hydrochloric acid, and the liberated fatty acids separately examined.

The Liquid Acids.—These acids, when distilled under diminished pressure, passed over between 235° and 250°/15 mm. as a yellow oil. An analysis and determination of the constants gave the following results:

0·1026 gave 0·2906 CO_2 and 0·1099 H_2O. C = 77·2; H = 11·9.

0·2646 absorbed 0·4120 iodine. Iodine value = 155·7.

0·3094 neutralised 0·0621 KOH. Neutralisation value = 200·7.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. I.V. = 90·1; N.V. = 198·9.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. I.V. = 181·4; N.V. = 200·4.

$C_{18}H_{30}O_2$ requires C = 77·7; H = 10·8 per cent. I.V. = 274·1; N.V. = 201·8.

These results would indicate that the liquid acids consist of a mixture of oleic, linolic, and linolenic acids.

The Solid Acids.—These acids, when crystallised from glacial acetic acid, separated in glistening leaflets, melting at 60—62°:

0·1030 gave 0·2875 CO_2 and 0·1194 H_2O. C=76·1; H=12·9.
0·2292 neutralised 0·0461 KOH. Neutralisation value=201·1.
$C_{16}H_{32}O_2$ requires C=75·0; H=12·5 per cent. N.V.=219·1.
$C_{18}H_{36}O_2$ „ C=76·1; H=12·7 „ „ N.V.=197·5.

The solid acids would thus appear to consist of a mixture of palmitic and stearic acids, the latter predominating.

Ethereal Extract of the Resin.

This extract, after the removal of the solvent, formed a brittle mass, which could readily be reduced to a light brown powder, and amounted to 75 grams. It was heated with 2 litres of alcohol when the greater portion dissolved. The small insoluble portion (2·3 grams) was collected, and identified as ipuranol.

Isolation of a New Lactone, Casimirolid, $C_{24}H_{28}O_6$.

The above-mentioned hot alcoholic liquid deposited on cooling a quantity (22·1 grams) of well-developed crystals, which, when recrystallised from alcohol with the addition of a little animal charcoal, separated in colourless prisms, melting at 229—230°:

0·0960 gave 0·2448 CO_2 and 0·0594 H_2O. C=69·5; H=6·9.
0·1326, in 21·16 benzene, gave Δt – 0·072°. M.W.=426.
$C_{24}H_{28}O_6$ requires C=69·9; H=6·8 per cent. M.W.=412.

From these results it is evident that the above-described substance possesses the formula $C_{24}H_{28}O_6$, and that it is a new compound. Having ascertained that it is a lactone, as shown below, it is proposed to designate it *casimirolid*.

Casimirolid is readily soluble in ether, chloroform, and ethyl acetate. It is optically active, and a determination of its specific rotatory power gave the following result:

0·3856, made up to 25 c.c. with chloroform, gave α_D – 1°31′ in a 2-dcm. tube, whence $[\alpha]_D$ – 49·2°.

Hydrolysis of the Lactone.

Formation of a New Hydroxy-acid, Casimiroic Acid, $C_{23}H_{28}O_4(OH)\cdot CO_2H$.

When casimirolid is shaken with a cold solution of potassium hydroxide in aqueous alcohol, it readily takes up a molecule of water, and is converted into an acid, which is precipitated on acidifying the alkaline liquid. This acid crystallises very readily from alcohol in rosettes of glistening needles, melting at 207°:

0·1074 gave 0·2638 CO_2 and 0·0698 H_2O. C=67·0; H=7·2.
0·2792 neutralised 0·0359 KOH. M.W.(monobasic acid)=436.

$C_{24}H_{30}O_7$ requires C=67·0; H=7·0 per cent. M.W.=430.

The above-described acid is thus shown to possess the formula $C_{24}H_{30}O_7$. Like the corresponding lactone, it is a new compound, and it is proposed to designate it *casimiroic acid.*

A determination of the optical rotatory power of the acid gave the following result:

0·1670, made up to 20 c.c. with absolute alcohol, gave α_D $-1°27'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-86·8°$.

Casimiroic acid, unlike the lactone, is very sparingly soluble in ether, chloroform, and ethyl acetate. Its sodium salt is very readily soluble in water and in alcohol. On the addition of a solution of copper sulphate to a neutral solution of the sodium salt, a pale blue, amorphous precipitate of copper casimiroate was produced, the analysis of which, however, indicated it to consist of a basic salt.

Silver Casimiroate, $C_{23}H_{29}O_5\cdot CO_2Ag$.—This salt was obtained as a white, amorphous precipitate on the addition of a solution of silver nitrate to a solution of the sodium salt. It is sparingly soluble in water, and gradually darkens on exposure to light:

0·1435 of salt gave, on ignition, 0·0296 Ag. Ag=20·6.

$C_{24}H_{29}O_7Ag$ requires Ag=20·1 per cent.

Methyl Casimiroate, $C_{23}H_{29}O_5\cdot CO_2\cdot CH_3$.—This ester was prepared by passing dry hydrogen chloride into a solution of the acid in methyl alcohol at the boiling temperature. It was very soluble in alcohol, and could only be obtained with difficulty in a crystalline state from dilute alcohol, when it melted at 108—110°:

0·1086 gave 0·2666 CO_2 and 0·0739 H_2O. C=66·9; H=7·6.

$C_{25}H_{32}O_7$ requires C=67·5; H=7·2 per cent.

Acetylcasimiroic Acid, $C_{23}H_{28}O_4(O\cdot CO\cdot CH_3)\cdot CO_2H$.—This was obtained by heating casimiroic acid with acetic anhydride, pouring the product into water, and digesting the resulting precipitate with dilute aqueous sodium carbonate, when, on acidifying the alkaline liquid, the *acetyl* derivative was precipitated. It was exceedingly soluble in the usual organic solvents, but could be obtained from dilute alcohol in colourless, microscopic needles. The acetyl derivative has no sharp melting point, but gradually decomposes at temperatures above 142°:

0·1149 gave 0·2774 CO_2 and 0·0738 H_2O. C=65·8; H=7·1.

$C_{26}H_{32}O_8$ requires C=65·8; H=6·8 per cent.

Isolation of a Yellow Phenolic Substance, $C_{16}H_{12}O_6$.

After the separation of the lactone, casimirolid, from the alcoholic solution of the ethereal extract of the resin, as previously described, the solvent was removed, and the residue, which still contained a small amount of lactone, dissolved in ether. The ethereal liquid was then successively extracted with solutions of ammonium carbonate, sodium carbonate, and sodium hydroxide. The ammonium carbonate removed only a small amount of resinous substance, from which nothing definite could be isolated. The sodium carbonate extract also consisted chiefly of resinous material, but by digesting the latter with alcohol, in which the resin was very soluble, a small amount (0·15 gram) of a crystalline substance was isolated. This substance, when recrystallised from dilute alcohol, separated in small, yellow needles, melting at 215—218°. Its solution gave a yellow colour with alkalis and with ferric chloride. With concentrated sulphuric acid it yielded an orange-red solution, slowly changing to pale yellow, but showing no fluorescence:

0·0816 gave 0·1904 CO_2 and 0·0290 H_2O. C=63·6; H=3·9.

$C_{16}H_{12}O_6$ requires C=64·0; H=4·0 per cent.

The *substance* thus appears to possess the formula $C_{16}H_{12}O_6$, but the amount available did not permit of its further characterisation. Although isomeric with the flavone derivatives, kæmpferid (*Ber.*, 1881, **14**, 2385) and the luteolin monomethyl ether prepared synthetically by Diller and Kostanecki (*Ber.*, 1901, **34**, 1452), it is not identical with either of these compounds.

The sodium hydroxide extract of the above-mentioned ethereal liquid yielded on acidification a quantity (4·2 grams) of a crystalline substance, which, when recrystallised from alcohol, separated in glistening needles, melting at 207°. This substance was identified as the previously described casimiroic acid, which had evidently been formed by the action of the alkali on the lactone present in the ethereal liquid. After the successive extraction of the ethereal liquid with the above-mentioned alkalis, the solvent was evaporated, but only a slight, oily residue remained.

Chloroform, Ethyl Acetate, and Alcohol Extracts of the Resin.

The chloroform extract of the resin formed a hard, black mass, and amounted to 18·6 grams. The only crystalline substance obtained from it was a small quantity (0·6 gram) of the previously described alkaloid, casimiroine. The ethyl acetate and alcohol

extracts were dark-coloured products, and amounted to 3·2 and 22 grams respectively. Both of these extracts were heated with 5 per cent. sulphuric acid in aqueous alcohol, but they yielded nothing definite, although the aqueous liquid resulting from this treatment of the alcohol extract evidently contained some sugar, for it readily reduced Fehling's solution, and from the liquid, after the removal of the sulphuric acid, a little *d*-phenylglucosazone (m. p. 206°) was prepared.

II.—*Examination of the Shells.*

A small portion (10 grams) of the ground shells was subjected to a preliminary test for an alkaloid by digestion with Prollius' fluid. The reactions obtained were much less marked than in the case of the kernels, but indicated the presence of a small amount of alkaloidal substance.

Another portion (50 grams) of the ground material was successively extracted with various solvents, when the following amounts of extract, dried at 100°, were obtained:

Petroleum (b.p. 35—50°)	extracted	0·2	gram	=	0·4	per cent.
Ether	,,	0·3	,,		0·6	,,
Chloroform	,,	0·1	,,		0·2	,,
Ethyl acetate	,,	0·1	,,		0·2	,,
Alcohol	,,	0·8	,,		1·6	,,
	Total......	1·5	grams	=	3·0	per cent.

For a complete examination of the shells a quantity (10·39 kilograms) of the ground material was completely extracted with hot alcohol. After the removal of the greater portion of the solvent, a thin extract, amounting to 482 grams, was obtained.

The whole of the above-mentioned extract was first distilled in a current of steam, when it yielded a very small amount (0·65 gram) of an essential oil. This oil appeared to be similar in character to that obtained from the kernels of the seed, but the amount was not sufficient for its further examination.

The aqueous liquid and resinous material remaining after the above-described treatment of the extract were examined by methods similar to those described in connexion with the kernels of the seed.

The chief constituents of the aqueous liquid were found to be amorphous colouring matter and sugar, the latter yielding *d*-phenylglucosazone, melting at 206°. No other crystalline product could be obtained from the liquid, the amount of alkaloidal substance present having proved to be too small to permit of its isolation.

The resinous material, when thoroughly washed and dried, formed a light brown, friable mass, and amounted to 95 grams, or about 0·9 per cent. of the weight of shells employed. The resin was

successively extracted with various solvents, and the resulting products separately examined. The petroleum extract, which amounted to 37 grams, contained a considerable quantity (20 grams) of stearic acid in a free state, together with a little free palmitic acid, and a small amount of these acids in the form of glycerides. The stearic acid, when crystallised from alcohol, separated in pearly leaflets, melting at 67—68°. (Found, C=76·2; H=13·1. Calc., C=76·1; H=12·7 per cent.) The ether, chloroform, ethyl acetate, and alcohol extracts of the resin amounted to 8·8, 30·4, 1·5, and 14·5 grams respectively, and consisted entirely of amorphous products. The chloroform and alcohol extracts were heated with 5 per cent. sulphuric acid in aqueous alcohol, but as they yielded no sugar by this treatment, they were not glucosidic in character.

Physiological Tests.

In order to ascertain whether either the hypnotic or toxic action attributed to *Casimiroa* seed (*loc. cit.*) could be confirmed, a number of tests were kindly conducted for us at the Wellcome Physiological Research Laboratories by Drs. H. H. Dale and P. P. Laidlaw, to whom our best thanks may here be expressed. All the products, with the exception of the essential oil, as noted below, were administered to dogs by the mouth.

The finely-divided kernel of an entire seed, weighing about 2 grams, as also 1 gram of the dry enzyme or protein material obtained from the seed, and representing 90 grams of the kernel had no effect. One gram of the alcoholic extract, representing 3·2 grams of the kernels of the seed, produced vomiting and a temporary depression, which was apparently due to the repeated emesis, but no other effect could be observed. A similar effect was produced by the administration of 1 gram each of the petroleum and alcohol extracts of the resin, whereas the ether, chloroform and ethyl acetate extracts of the resin were inactive. The following crystalline substances which had been isolated from the seed namely, casimiroine, $C_{21}H_{20}O_8N_2$, casimiroedine, $C_{17}H_{24}O_5N_2$, and the lactone, casimirolid, $C_{24}H_{28}O_6$, were given to dogs in amounts of 0·4 gram, and also to cats in doses of 0·1 gram respectively, but the animals remained perfectly normal. Inasmuch as the experiments of Chevalier (*loc. cit.*) led him to conclude that the therapeutic value of *Casimiroa* seed is due to the essential oil or the resin which he presumed to be produced therefrom, a special test was conducted with the essential oil. A quantity (0·25 c.c.) of this product representing about 1100 grams of the kernels of the seed when given to a cat, produced salivation and slight depression

which may be ascribed to the nauseating taste of the substance, but there was no further effect, and particularly no trace of narcosis.

Summary.

The material employed for this investigation consisted of the fresh seeds of *Casimiroa edulis*, La Llave and Lejarza (Nat. Ord. *Rutaceae*), which were obtained directly from Mexico.

For the purpose of their examination, the kernels of the seed were first separated from the dry, fibrous shells. The latter, which represented about one-fifth the weight of the entire fresh seed, were separately examined, but yielded little of interest. They were found to contain a small amount of an essential oil, traces of alkaloidal substance, some sugar, and considerable stearic acid in the free state, together with resinous material.

The kernels of the seed, when subjected to a preliminary test, gave reactions indicating the presence of a considerable proportion of an alkaloid. They were also found to contain an enzyme, which was obtained in the form of a light brown powder, and slowly effected the hydrolysis of amygdalin.

An alcoholic extract of the ground kernels, when distilled in a current of steam, yielded a small amount of a pale yellow essential oil, which gradually darkened in colour. This oil had an agreeable, aromatic odour, and the following constants: $d = 0{\cdot}9574$ at 20°; $a_D + 2°25'$ in a 25 mm. tube.

From the portion of the extract which was soluble in water there were isolated: (i) a new alkaloid, *casimiroine*, $C_{24}H_{20}O_8N_2$ (m. p. 196–197°), which is a very weak base, but yields a crystalline *picrate* (m. p. 165°) and an *aurichloride* (m. p. 195—196°). On heating casimiroine with alkalis, it undergoes hydrolysis, with the elimination of carbon dioxide, yielding a new base, *casimiroitine*, $C_{23}H_{22}O_7N_2$ (m. p. 171°), together with a small amount of a basic substance melting at 159°; (ii) a new alkaloid, *casimiroedine*, $C_{17}H_{24}O_5N_2$ (m. p. 222—223°; $[a]_D$, in acid solution, $-36{\cdot}5°$), which yields a crystalline *aurichloride*; (iii) benzoic acid, with apparently a trace of salicylic acid. The aqueous liquid contained, furthermore, a quantity of sugar, which yielded *d*-phenylglucosazone (m. p. 205—207°).

The portion of the alcoholic extract which was insoluble in water consisted of a soft, oily resin. From this material the following compounds were isolated: (i) sitosterol, $C_{27}H_{46}O$ (m. p. 134—135°; $[a]_D - 32{\cdot}1°$); (ii) ipuranol, $C_{23}H_{38}O_2(OH)_2$; (iii) a mixture of fatty acids, consisting of palmitic, stearic, oleic, linolic, and linolenic acids; (iv) a new lactone, *casimirolid*, $C_{24}H_{28}O_6$ (m. p. 229—230°; $[a]_D - 49{\cdot}2°$), which yields a new hydroxy-acid, designated as

casimiroic acid, $C_{23}H_{28}O_4(OH)\cdot CO_2H$ (m. p. 207°; $[\alpha]_D$ −86·8°. The following derivatives of this acid were prepared: *silver casimiroate*, $C_{22}H_{29}O_5\cdot CO_2Ag$; *methyl casimiroate*, $C_{23}H_{29}O_5\cdot CO_2CH_3$ (m. p. 108—110°); and *acetylcasimiroic acid*,

$$C_{23}H_{28}O_4(O\cdot COCH_3)\cdot CO_2H;$$

(v) a yellow, phenolic *substance*, $C_{16}H_{12}O_6$ (m. p. 215—218°).

It may finally be noted that the results of the present investigation of *Casimiroa* seed have afforded no evidence of the presence of a definite glucoside or a so-called "glucoalkaloid," as has previously been affirmed, and physiological tests conducted with animals have likewise failed to confirm their reputed hypnotic or toxic properties.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXXVII.—*Komppa's Synthesis of Camphoric Acid.*

By GUSTAVE LOUIS BLANC and JOCELYN FIELD THORPE.

THE publication of Komppa's reply to our criticism respecting his synthesis of camphoric acid (this vol., p. 29) has led us to investigate the action of very dilute alkali on methyl diketocamphorate (I). Under these conditions the compound is converted into the alkali salt of the dibasic acid, which eliminates carbon dioxide when acidified, and yields the monobasic acid (II). This substance passes into the diketone (III) when it is heated at 160°:

$$\begin{matrix}CO\cdot CMe(CO_2Me)\\ |\\ CO-CH(CO_2Me)\end{matrix}\!>\!CMe_2 \longrightarrow \begin{matrix}CO\text{——}CHMe\\ |\\ CO\cdot CH(CO_2H)\end{matrix}\!>\!CMe_2 \longrightarrow$$

(I.) (II.) (M. p. 146°.)

$$\begin{matrix}CO\cdot CHMe\\ |\\ CO-CH_2\end{matrix}\!>\!CMe_2$$

(III.) (M. p. 83°.)

The lower homologue of this diketone (IV) is prepared by distilling methyl diketo*apo*camphorate with dilute sulphuric acid:

$$\begin{matrix}CO\cdot CH(CO_2Me)\\ |\\ CO\cdot CH(CO_2Me)\end{matrix}\!>\!CMe_2 \longrightarrow \begin{matrix}CO\cdot CH_2\\ |\\ CO\cdot CH_2\end{matrix}\!>\!CMe_2$$

(IV.) (M. p. 45°.)

The two diketones were characterised by the formation of the osazones and dioximes.

There is, then, no question that under the experimental condi-ions used by Komppa for the reduction of methyl diketocamphorate* he methyl group remains attached to carbon; our criticism of his ynthetical formation of camphoric acid is therefore baseless.

Experimental.

3:4-*Diketo*-1:1:2-*trimethyl*cyclo*pentane*-5(or 2)-*carboxylic Acid*,

$$\left.\begin{array}{l} CO\text{——}CHMe \\ CO\cdot CH(CO_2H) \end{array}\right> CMe_2 \quad \text{or} \quad \left.\begin{array}{l} CO\cdot CMe(CO_2H) \\ CO\text{———}CH_2 \end{array}\right> CMe_2.$$

Five grams of methyl diketocamphorate were dissolved in a olution containing rather more than the theoretical amount of otassium hydroxide in ten times its weight of water, and allowed o remain at the ordinary temperature for twenty-four hours; the olution was then evaporated in a desiccator to half its volume, and cidified by hydrochloric acid. Carbon dioxide was eliminated, and he monobasic acid slowly separated; it was recrystallised from vater at 50°, and obtained in small, flattened needles, melting at 146°, with immediate evolution of carbon dioxide:

0·2267 gave 0·4864 CO_2 and 0·1289 H_2O. C = 58·51; H = 6·37.

$C_9H_{12}O_4$ requires C = 58·7; H = 6·5 per cent.

3:4-*Diketo*-1:1:2-*trimethyl*cyclo*pentane*,

$$\left.\begin{array}{l} CO\cdot CHMe \\ CO\text{—}CH_2 \end{array}\right> CMe_2.$$

This diketone is formed when the above acid is heated in a bath of sulphuric acid at 160° until carbon dioxide ceases to be evolved. It crystallises from water containing a little alcohol in long, silky needles, which melt at 83°:

0·2098 gave 0·5260 CO_2 and 0·1620 H_2O. C = 68·42; H = 8·61.

$C_8H_{12}O_2$ requires C = 68·6; H = 8·6 per cent.

Like the similar compounds investigated by Dieckmann (*Ber.*, 1902, **35**, 3208), this substance is largely, if not entirely, enolic in structure; thus it gives a violet coloration with ferric chloride, and readily dissolves in aqueous potassium hydroxide, yielding a potassium salt, which is sparingly soluble in excess of alkali. It reacts, however, towards phenylhydrazine and hydroxylamine as a diketone.

The *osazone*, prepared in acetic acid solution, separates from alcohol containing a little water in small, yellow prisms, which melt at 162°:

0·1507 gave 22·1 c.c. of N_2 at 14° and 747 mm. N = 17·2.

$C_{20}H_{24}N_4$ requires N = 17·5 per cent.

The *dioxime* separates after some days from a solution of the ketone and hydroxylamine hydrochloride in dilute alcohol containing the theoretical amount of potassium hydroxide. It crystallises from dilute alcohol in long, slender needles, which melt and decompose at 172°:

0·1200 gave 0·2476 CO_2 and 0·0907 H_2O. C=56·32; H=8·21.

$C_8H_{14}O_2N_2$ requires C=56·3; H=8·4 per cent.

The diketone is soluble in water, and when pure can be recrystallised from this solvent; the aqueous solution is neutral to litmus. It completely sublimes at 70° without melting.

3:4-*Diketo*-1:1-*dimethyl*cyclo*pentane*,

$$\begin{matrix} CO\cdot CH_2 \\ | \\ CO\cdot CH_2 \end{matrix}\!\!>CMe_2.$$

The preparation of this substance can be effected by boiling methyl diketo*apo*camphorate with dilute sulphuric acid (one of acid to three of water) for three hours, and distilling the product with steam. The diketone passes over as an oil, which boils at 197°/748 mm., and yields a distillate, which solidifies to a mass of needles on cooling. It melts at 45°, and is readily soluble in all organic solvents:

0·2279 gave 0·5541 CO_2 and 0·1591 H_2O. C=66·52; H=7·83.

$C_7H_{10}O_2$ requires C=66·7; H=7·9 per cent.

The *osazone*, prepared in acetic acid solution, separates as an oil which resinifies on keeping. It can be obtained crystalline by rubbing with alcohol, and recrystallising from this solvent; it forms yellow needles, melting at 167°:

0·1355 gave 21·4 c.c. of N_2 at 16° and 746 mm. N=18·32.

$C_{19}H_{22}N_4$ requires N=18·3 per cent.

The enolic structure of this diketone is apparent from the fact that it gives a deep wine-red colour with ferric chloride, and dissolves in aqueous potassium hydroxide, yielding a solution from which excess of alkali precipitates the potassium salt in glistening plates. The potassium salt is readily soluble in water. and the solution deposits the diketone when acidified. The aqueous solution of the diketone is faintly acid to litmus.

THE SORBONNE,
PARIS.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXXVIII.—*The Lower Limit of Inflammation of Mixtures of the Paraffin Hydrocarbons with Air.*

By MAURICE JOHN BURGESS and RICHARD VERNON WHEELER.

WHEN a source of heat, such as a lamp flame or an electric spark, is introduced into a mixture of a combustible gas and air, two things are necessary to ensure propagation of flame throughout that mixture.

Supposing that too small a proportion of combustible gas is present, only a small quantity of heat per unit volume of mixture is liberated when the layer surrounding the initial source of heat is inflamed, and the products of combustion have to impart heat to a considerable volume of "inert" gases. The number of collisions between molecules of combustible gas and of oxygen that are chemically fruitful is therefore small. Such collisions, resulting in combination, will occur only in the neighbourhood of the initial source of heat, around which an aureole or "cap" will form of a size dependent on the nature and quantity of the combustible gas present.

As the proportion of combustible gas is increased, a greater quantity of heat is evolved per unit volume of mixture, and a smaller volume of inert gases is present to absorb it; until a point is reached when the amount of heat contained in the products of combustion of any given layer is just sufficient to raise to its ignition-temperature* the layer adjacent. Flame is then propagated from layer to layer throughout the mixture without any necessity for the continued presence of the source of heat which started the inflammation, and the mixture is said to "inflame" or "explode" according to the rapidity of the propagation.

To ensure propagation of flame, therefore, it is necessary (1) that the initial source of heat should be of a volume, intensity, and duration sufficient to raise the layer of gases in its immediate vicinity to a temperature higher than, or as high as, the ignition-temperature of the mixture; and (2) that the heat contained in the products of combustion of this first layer should be sufficient to raise the adjacent layer to its ignition-temperature.

The smallest quantity of any combustible gas which, when mixed with a given quantity of air (or oxygen), will enable this self-propagation of flame to take place, is termed the *lower limit of inflammation* of the gas.

* By "ignition-temperature" we mean, accepting Nernst's definition, that temperature at which rapid self-heating of the mixture takes place.

Similarly, there is a *higher limit* of inflammation corresponding with the greatest quantity of inflammable gas, or, rather, with the smallest quantity of oxygen, that will allow self-propagation of flame. The experimental part of this paper deals only with the lower limit.

The first systematic determinations of the limits of inflammation were made in 1816 for "firedamp" by Davy, who thus describes them ("Collected Works," Vol. VI., p. 24): "When 1 part of firedamp was mixed with 1 of air, they burnt by the approach of a lighted taper, but did not explode; 2 of air and 3 of air to 1 of gas produced similar results. When 4 of air and 1 of gas were exposed to a lighted candle, the mixture being in the quantity of 6 or 7 cubical inches in a narrow-necked bottle, a flame descended through the mixture, but there was no noise; 1 part of gas inflamed with 6 parts of air in a similar bottle, produced a slight whistling sound; 1 part of gas with 9 parts of air, rather a louder sound; 1 part with 10, 11, 12, 13, and 14 parts, still inflamed, but the violence of combustion diminished. In 1 part of gas and 15 parts of air, the candle burnt without explosion with a greatly enlarged flame; and the effect of enlarging the flame, but in a gradually diminishing ratio, was produced as far as 30 parts of air to 1 of gas."

These experiments, therefore, place the lower limit of inflammation of the particular sample of "firedamp" that Davy used as between 6·3 and 6·7 per cent.

Davy's determinations were repeated in 1876 by Coquillon (*Compt. rend.*, 1876, **83**, 709), who ignited the mixture in a closed vessel by means of an electric spark. His results, and his description of them, are similar to Davy's, but he places the lower limit at about 5·8 per cent.

Later determinations of the limits of inflammation of "firedamp," and of a number of pure gases and vapours, have been made by Le Chatelier, in conjunction with Mallard (*Ann. des Mines*, 1883, [illegible]) and Boudouard (*Compt. rend.*, 1898, **126**, 1344 and 1510). The figure given for firedamp (assumed to be pure methane) is 6·0 per cent. This figure has received general acceptance throughout the coal-mining world, to which it is, of course, of paramount importance.

The most recent results that have come to our notice are those published by Teclu (*J. pr. Chem.*, 1907, [ii], **75**, 212). Teclu states that the lower limit of inflammation of methane, prepared from sodium acetate, lies between 3·20 and 3·67 per cent.*

* Since this was written a letter from Dr. E. P. Perman has appeared in the correspondence columns of *Nature* (September 28th, 1911) entitled "Limits of

In connexion with the work on coal-dust explosions on which we have been engaged for the Mining Association of Great Britain, it was essential that we should know with certainty what was the smallest amount of firedamp which, when present in dust-free air at ordinary temperature and pressure, would enable flame to be propagated when a source of heat was introduced. Teclu's results differed so widely from those generally accepted that we found it necessary to make fresh determinations under conditions which would as far as possible eliminate sources of error such as cooling by the walls of the vessel in which the inflammable mixtures were ignited.

Moreover, we had reason to believe that "firedamp" should not be regarded as consisting of pure methane, or methane diluted with a greater or lesser quantity of air, but that in many samples other hydrocarbons are present in appreciable (and by no means negligible) quantities.

In this connexion Davy says (*loc. cit.*, p. 14): "Though all the specimens of firedamp which I have examined consisted of carburetted hydrogen mixed with different small percentages of carbonic acid and common air, yet some phenomena that I observed in the combustion of a blower induced me to believe that small quantities of olefient gas may be sometimes evolved in coal mines with the carburetted hydrogen."

A full discussion of the probable composition of firedamp as it exists in coal mines appears in a paper by Gray (*Trans. Inst. Mining Eng.*, 1910, **39**, 286), who points out that although methane is the only inflammable gas that has been reported as contained in firedamp in the large number of analyses that have been made in the last few years, yet since the proportion of firedamp in the atmosphere of a well-ventilated mine is usually small, it is quite likely that the relatively much smaller proportion of other inflammable gases has escaped recognition; and he places on record the analysis of a sample which contained noteworthy quantities of

Explosibility in Gaseous Mixtures." Dr. Perman states that he has obtained much wider limits than those usually given, and he gives for methane 2·5 per cent. as the lower limit of explosibility (inflammation) when mixed with air. Ignition was effected by means of an incandescent platinum wire, the experiments being carried out in a glass tube of about 10 c.c. capacity, having a stopcock at each end and a mercury gauge of small bore attached to the middle of the tube. Dr. Perman says: "when the explosion occurs the mercury moves more or less sharply, according to the force of the explosion, but a distinct movement, apart from that due merely to the expansion caused by the heating of the wire, can be seen with the proportions of gases given above." From the fact that a "distinct movement" of the mercury gauge could be observed, it does not necessarily follow that the mixture experimented with was explosive or even inflammable. The expansion caused by the heat of combustion of only a trace of inflammable gas would be sufficient to affect a sufficiently delicate gauge.

higher paraffins. If it is assumed that ethane was the only paraffin hydrocarbon present beside methane in this particular sample of firedamp, Gray's analysis shows that the combustible gas contained 55·5 per cent. of methane and 44·5 per cent. of ethane, the proportions present in the air mixture being 1·84 and 1·47 per cent. respectively.

Further, when it is remembered that the major portion of the inflammable gases that find their way into the ventilating current of coal mines issues from minute fissures in the coal,* and that the gases that can be extracted from coal at the ordinary temperature, either by exhaustion or by simply crushing, contain not only ethane but higher members of the paraffin series of hydrocarbons, it will be seen that the limits of inflammability of every sample of "firedamp" must not be regarded as identical with those of any one particular sample.

These considerations prompted us to determine the lower limit of inflammation of the higher members of the paraffin series of hydrocarbons when mixed with air, as well as that of methane. At the same time it appeared that it should be possible, by obtaining a sufficiency of data, to establish some definite relationship between the lower limit of inflammation of any gas and its known physical properties.

A "lower-limit mixture" is one such that a given volume must, under the conditions of its combustion, evolve just sufficient heat to raise an equal volume to its ignition-temperature. There are at least three factors which must obviously determine this necessary condition: (1) the calorific power of the gas; (2) the relative volume and specific heat of the diluent gases; and (3) the ignition-temperature of the mixture.

Of these three factors the first must undoubtedly exercise the preponderating influence; for, taking the paraffin series of hydrocarbons, C_nH_{2n+2}, when n is small the calorific value of the gas is much less than when n is large; so that, a priori, the higher the value of n the less volume of the gas need be present in air to form a lower-limit mixture. This means also that the higher the value of n the greater the volume of diluent gases present per unit volume of mixture. On the other hand, as is indicated by the determinations made by Dixon and Coward (Trans., 1909, **95**, 514), the

* Many investigations have been made regarding the nature of the gases that are contained in coal after it has been mined, when, presumably, considerable escape of gas has already occurred. Amongst the most important are those by von Meyer (*J. pr. Chem.*, 1872, [ii], **5**, 144, 407, **6**, 360), Thomas (*Journ. Chem. Soc.*, 1875, **28**, 793), and Bedson and McConnell (*Trans. Fed. Inst. Min. Eng.*, 1892, **3**, 307). More recently Porter and Ovitz (*U.S. Bureau of Mines, Tech. Paper*, 2, 1911) have conducted experiments with freshly-mined coal, and give some remarkable figures for the rate of escape of gases therefrom when crushed.

ignition-temperatures of the paraffin hydrocarbons appear to fall slightly as the series is ascended.

The effect of an increase in these two last-named factors is small in comparison with the effect of the increased calorific value of the gas, and they operate in a contrary direction.

As a first approximation, therefore, it would appear probable that the lower limit of inflammation should vary inversely as the calorific value of the gas; that is to say, if L = the proportion of the combustible gas necessary to form a lower limit mixture, and C = its calorific value,

$$L = f(1/C), \text{ or, say, } L = k1/C \quad . \quad . \quad . \quad . \quad (1),$$

where k is a constant, the meaning of which will be considered later. Before considering its probable meaning, it will be of interest to see to what extent equation (1) is borne out by our experimental numbers.

The value that we have obtained for the lower limit of inflammation of methane when mixed with air is 5·6.* That is to say, the lower-limit mixture contains 5·6 per cent. by volume of methane. The calorific value of methane is 189·1.† Substituting in equation (1) we obtain a value for k of 1059, and the relative values for L for other gases can then be calculated.

In the table that follows the relative values of L are calculated from equation (1) in this manner, using methane as the standard to obtain the value of k. The observed values of L were obtained for the pure gases in the manner described in the experimental part of this paper. In every case the mixtures were ignited in a closed spherical vessel when at atmospheric pressure, and saturated with moisture at the room temperature (20—25°). The values are expressed as volumes of the inflammable gas per hundred volumes of mixture. In a separate column are given the lower calorific values of the gases at constant volume expressed in large calories per gram-molecule:

Gas.	Calorific value.	L observed.		L calculated.
Methane	189·1	5·60	standard	5·60
Ethane	336·6	3·10		3·15
Propane	484·2	2·17		2·19
n-Butane	631·7	1·65		1·68
n-Pentane	779·2	1·37		1·36
*iso*Pentane	779·2	1·32		1·36

* Throughout this paper, unless otherwise stated, the numbers given for the lower limits of inflammation are expressed as percentages by volume of the mixture of the combustible gas with air, and refer to mixtures at atmospheric temperature and pressure.

† The value used in the *lower* value (Thomsen) expressed in large calories per gram-molecule.

The agreement between the observed and calculated values of L is very striking, and seems to point to a definite and dominating relationship between the calorific values of the gases named in the table—the paraffin hydrocarbons—and their lower limits of inflammation when mixed with air.

If, however, it is attempted to calculate the lower limit for gases other than the paraffin hydrocarbons in the same way, using methane as the standard to obtain the value of k, the results do not all agree with experiment; thus, hydrogen, for which Le Chatelier gives an experimental value 10·0 ("Leçons sur le Carbone," p. 266), should have a value 18·45 according to equation (1). There is, therefore, some other factor to be considered.

This becomes apparent also on attempting to calculate the theoretical quantities of gas that are necessary to obtain a lower-limit mixture, assuming the reaction on ignition to take place adiabatically.

If T = the temperature of ignition of the mixture;
t = the initial temperature;
c' = the specific heat at constant volume of air;
c'' = the specific heat at constant volume of the combustible gas;
x = the amount of combustible gas present by weight;
$100 - x$ = the amount of air present by weight;
Q = the heat evolved by one part by weight of the combustible gas;

then:

$$[(100 - x)c' + xc''](T - t) = Qx,$$

or:

$$x = \frac{100c'(T - t)}{Q - (c'' - c')(T - t)}.$$

The value of $(c'' - c')(T - t)$ can be neglected compared with that of Q, being of the order of 1 part in 1000. So that, if $t = 0$, the equation becomes:

$$x = \frac{100c'T}{Q} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2).$$

In attempting to use this equation for the calculation of the quantities of the paraffin hydrocarbons necessary, one is faced with the difficulty that their ignition-temperatures are very ill-defined; thus, Dixon and Coward (*loc. cit.*, p. 519) give the following figures for methane, ethane, and propane burning in oxygen:

Methane	between	556	and	700°
Ethane	,,	520	,,	630
Propane	,,	490	,,	570

and reference to the experimental part of their paper shows that in the case of all three gases peculiarities were noticed for which

no satisfactory explanation was offered. Their behaviour was, however, similar in many respects, and seemed to indicate an unduly prolonged period of slow, flameless combustion before ignition took place.

All things considered, the lower values seem to be the best to choose for the purpose of calculating the lower limits; for we wish to know the least amount of heat required.

For these three gases, the only members of the paraffin series of which Dixon and Coward have determined the ignition-temperatures, we have calculated the lower-limit values from equation (2), using the gram and the large calorie as units, and taking the specific heat of air at constant volume as 0·169.

Gas.	Percentage by weight required to form a lower-limit mixture.	Percentage by volume.	
		Calculated.	Observed.
Methane	0·795	1·426	5·60
Ethane	0·783	0·754	3·10
Propane	0·753	0·495	2·17

That the calculated values should be smaller than the observed is easily explained by the fact that the reaction that takes place on ignition has been assumed to be adiabatic, whereas actually heat is bound to be communicated from the gases first inflamed, not only to the adjacent layer, but to layers at a further distance. The amount of heat transmitted in this way must be determined chiefly by the speed at which the flame is propagated; for the more rapidly each successive layer is raised to its ignition-temperature the less will be the quantity of heat dissipated throughout more distant layers or through the walls of the containing vessel. Further than this, a certain proportion of the energy liberated during the reaction appears as radiant energy, and is not imparted to the products of combustion as sensible heat.

In the case of the three paraffin hydrocarbons, methane, ethane, and propane, the observed quantities required to form lower-limit mixtures with air are about four times the calculated quantities. In the case of hydrogen, however, the calculated quantity is 5·92, whilst the observed (Le Chatelier) is 10·0; that is to say, only about one and three-quarter times as great. The factors, therefore, other than the calorific value of the gas, which determine the quantity necessary to form a lower-limit mixture, operate in a different degree in the case of the paraffin hydrocarbons from what they do in the case of hydrogen or, no doubt, other inflammable gases.

From the fact that for all the paraffin hydrocarbons experimented with these factors taken together assume a constant value [as shown by the close agreement of equation (1) with experiment], it would appear that the mechanism of combustion of the inflammable gas

plays an all-important part in determining the quantity necessary to form a lower-limit mixture. For in the case of the paraffins the chemical changes resulting in inflammation are of a similar nature, the result of the initial encounter between the molecules of hydrocarbon and oxygen being, in each case, the formation of an oxygenated molecule; thus Bone and Wheeler (Trans., 1902, 81, 536; 1903, **83**, 1074) have shown that unstable intermediate products are formed during the slow combustion of methane, according to the following scheme of reaction:

1. $CH_4 + O_2 = H{\cdot}CHO + H_2O$.
   Formaldehyde.

2. (*a*) $H{\cdot}CHO + O_2 = CO_2 + H_2O$.
   (*b*) $2H{\cdot}CHO + O_2 = (2H{\cdot}CO_2H) = 2CO + 2H_2O$.

Similarly, in the case of ethane, Bone and Stockings (Trans., 1905, **87**, 1232) have shown that formaldehyde and acetaldehyde are formed as intermediate products during slow combustion (see also Bone and Drugman, Trans., 1906, **89**, 660).

In our experiments we have found that whenever the mixture contained less of the particular paraffin hydrocarbon used than was required to enable self-propagation of flame to take place, the water contained in the spherical explosion vessel gave an aldehydic reaction with Schiff's reagent; but that after a lower-limit mixture had been ignited no aldehydes could be detected. In the latter case the heat of reaction destroyed the aldehydes as soon as formed; in the former, where the flame burned only in the vicinity of the electric spark, the intermediate products of combustion had time to diffuse away to the cool parts of the containing vessel.

This mode of combustion "by stages" of the paraffins is to our mind a sufficient explanation of the difficulty that Dixon and Coward experienced in fixing a definite ignition-temperature for methane, ethane, and propane *; and it suggests a reason why, since their behaviour on oxidation is similar, the calorific value of the paraffins is the sole determining factor in calculating the relative lower limits of inflammation of mixtures of each with air.

Experimental.

The method of experiment that we have adopted has been that of passing an electric spark from an induction coil between ter-

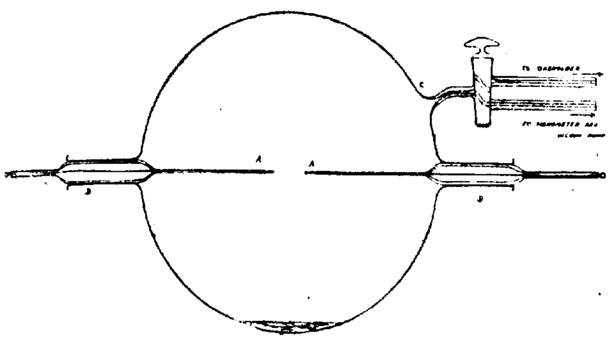
* Professor Dixon informs us that during the experiments made to obtain the ignition-temperatures of methane, ethane, and propane, a powerful odour of aldehyde was always noticed just before the gases inflamed, and that in some experiments the production of aldehyde seemed to be continued over a prolonged period at temperatures which in other experiments were sufficient to inflame the gases.

minals placed at the centre of the mixture of inflammable gas and air contained in a spherical vessel of about 2 litres capacity.

Previous workers have generally used an eudiometer tube of the diameter usually employed in the explosion analysis of gases; and have ignited the mixture either by passing an electric spark between platinum electrodes fused into the glass at one end of the tube, or by holding a lighted candle or taper to an open end of such a tube, the other end being closed. In either case the lower-limit mixture has been taken to be that in which the flame just travelled from one end of the tube to the other.

We considered that the cooling effect of the walls of such tubes may have influenced to some extent the results obtained, and therefore decided to use the spherical vessel above-mentioned, in

FIG. 1.



which the cooling by the walls would be reduced to a minimum. This method of experiment would also, it was thought, approximate more nearly to the conditions under which accidental ignitions of firedamp may take place in mines. We wished, moreover, to obtain some evidence of the influence, if any, of the size and intensity of the source of heat used to cause ignition, and of small variations in the initial temperature and pressure of the mixtures, on their lower-limit values.

The apparatus used is shown diagrammatically in Fig. 1. It consisted of a stout-walled glass globe nearly 16 cm. in diameter, with a capacity of just under 2 litres. The electrodes *A A*, which could reach to the centre, were platinum knobs, 3 mm. in diameter carried by stout platinum wires (coated with glass) along a diameter of the globe, passing by means of the parallel-ground joints, *B B*, through its walls. Each electrode, by reason of this

ground-glass connexion to the globe, could move horizontally through a distance of 3 cm., thereby allowing a maximum spark-gap of 6 cm. to be used. These "parallel" joints were made from accurately-ground hypodermic syringes, and, when lubricated with a solution of indiarubber in vaselin, maintained a vacuum during several hours.

Entrance to the globe was obtained through the tubulure *C*, to which was sealed a three-way tap of the form shown in the diagram. One branch of this tap made connexion with a glass gas-holder, in which the mixture to be experimented with was stored, and the other led to a mercury syphon manometer and a vacuum pump.

In all but a few special experiments a little distilled water (about 5 c.c.) was placed in the globe to saturate the mixture with water-vapour at the room temperature.

Preparation of the Gas and Air Mixtures.—The mixtures were prepared by adding measured volumes of the pure combustible gases to air, free from carbon dioxide, contained in graduated gas-holders over concentrated sulphuric acid. The apparatus employed is shown in Fig. 2. The pure combustible gas, which was stored in large test-tubes over mercury, was transferred, by means of the mercury trough and syphon, *A*, to the measuring cylinder, *B*, which was accurately graduated, and a volume taken sufficient to give the percentage required when mixed with four litres of air contained in the gas-holder, *C*. After being allowed to remain twelve hours to diffuse, a sample of the mixture was withdrawn and an explosion analysis made, a little pure electrolytic gas being added to ensure a good explosion.

The pure gases were prepared by the following methods:

Methane.—By the modification of Gladstone and Tribe's method described by Bone and Wheeler (Trans., 1902, **81**, 541). The gas was freed from traces of hydrogen by passage through "oxidised" palladium sponge heated to 98°, and by subsequent liquefaction by means of liquid air. The ratio C/A obtained in explosion analyses was exactly 2·0, showing that the gas was quite free from hydrogen.

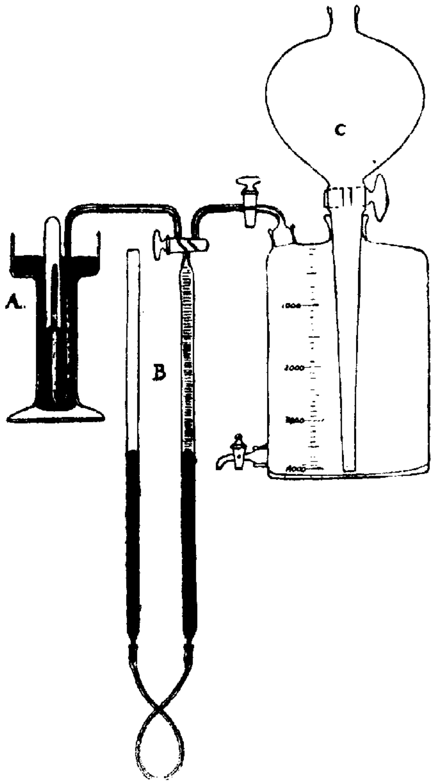
Ethane.—By the action of water on zinc ethyl. The gas was purified by several liquefactions with liquid air to remove traces of propane. The ratio C/A on explosion was 1·25 for one sample and 1·26 for another. (The ratio for pure ethane is 1·25.)

Propane and n-*Butane.*—By the action of nascent hydrogen (from zinc dust and dilute sulphuric acid) on the corresponding alkyl iodide. The gases were liquefied by cooling with solid carbon dioxide dissolved in ether, and fractionally distilled, the middle fraction only being collected. The sample of propane prepared

in this manner gave in an explosion analysis a ratio $C/A = 0{\cdot}99$; the sample of butane gave a ratio $= 0{\cdot}87$. (The ratios for pure propane and butane are 1·00 and 0·875 respectively.)

n-*Pentane and* iso*Pentane*.—The pure liquids were obtained from Kahlbaum, and a "stock" mixture of the vapour and air was

FIG. 2.



procured in each case by drawing dry air through the liquid contained in a wash-bottle maintained at 25°. In this manner mixtures containing high percentages of the hydrocarbon vapours were obtained; that of *n*-pentane and air containing 78·0 per cent. of *n*-pentane, and that of *iso*pentane and air containing 45·6 per cent. of *iso*pentane. The ratio C/A on explosion in the case of the

first-named was 0·81, and in the case of the second 0·80. (T ratio for pure pentane is 0·80.)

The pentane and air mixtures for the experiments were prep from these stock mixtures by further dilution with air.

The manner of determining the lower-limit mixtures was tha "trial and error"; for example, a mixture of methane and containing 6·1 per cent. of methane having been tried and fo to propagate inflammation on the passage of an electric spark second mixture was prepared containing 5·9 per cent. of meth This also propagated flame. The percentage of methane was the fore further reduced by 0·10 in a new mixture, and so on, until mixtures were obtained, differing in their content of methane 0·20 per cent., one of which enabled flame to be propagated, wh the other did not. The lower-limit mixture was taken to be th containing the mean percentage of methane contained in these mixtures.

The lower-limit mixture could be distinguished with certain from that just containing insufficient combustible gas; for the momentary passage of the electric spark sufficed to promote the inflammation of all the gas contained in the globe in the form case, and on further sparking no signs of combustion could be observed. Whilst in the latter case, although the flame of the burning gas might appear to travel nearly through the whole mixture on the first passage of the spark, and some doubt might exist as to whether it had not, in fact, travelled throughout, on causing the spark to pass a second time, a "cap" appeared above it, showing that the mixture still contained combustible gas, a this cap remained whilst passage of the spark was continu growing gradually smaller in size, until all the gas had be burnt.

As a further check, samples of the residual gases were withdra from the globe after experiments with mixtures near the low limit, and complete analyses made.

All the experiments were made in a darkened room, so as to enable the appearance of the flames to be readily observed.

Results of Experiments.—Before considering the influence of th size and nature of the source of heat used to cause ignition, or th effect of variations in the initial temperature and pressure of th mixtures, we will give the details of the experiments made wit the different gases when these conditions were constant.

For these experiments a spark-gap of 13 mm. was employed, th spark being obtained from a large induction coil. The initi pressure of the mixtures was between 760 and 765 mm., and th temperature between 20° and 25°. The gases were saturated wi water-vapour at this temperature.

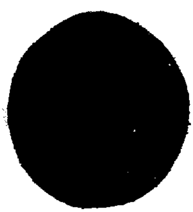
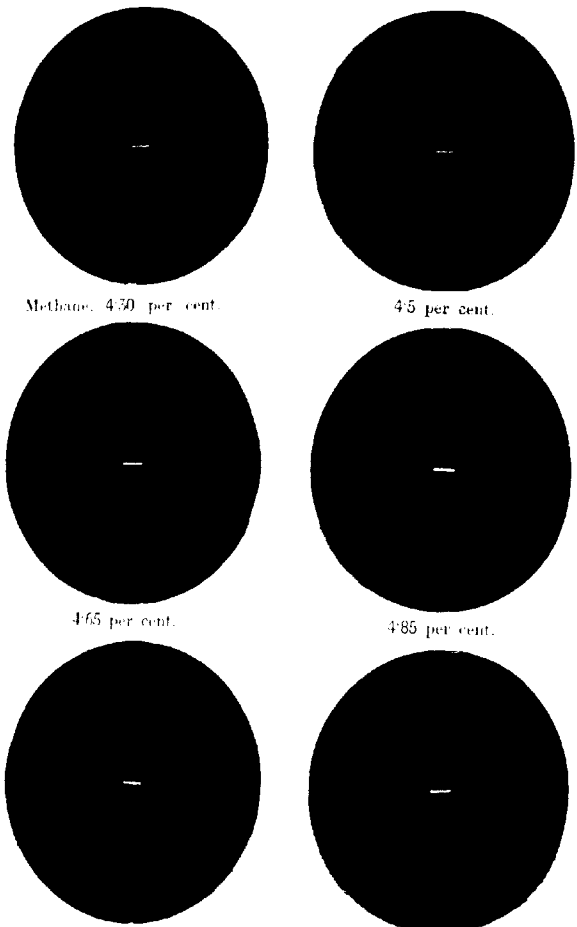


FIG. 3.



Methane. 4·30 per cent.

4·5 per cent.

4·65 per cent.

4·85 per cent.

5·00 per cent.

5·50 per cent.

[*To face p.* [illegible]]

Three, and sometimes four, experiments were made with the ixtures verging on the lower limit, the remainder being done in iplicate. The percentages of combustible gas recorded, deterined by explosion analysis, are correct within 0·05; that is to y, for example, a mixture recorded as containing 4·30 per cent. methane contained between 4·27 and 4·32 per cent.

Methane.

CH_4 present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
4·30	Small flame or "cap" above spark, about 3 cm. high	Size of cap slightly diminished
4·50	Flame about 6 cm. high above spark	Size of cap slightly diminished
4·65	Flame about 8 cm. high spreading sideways above spark	Size of cap diminished
4·85	Large flame spreading through about a quarter of the mixture	Size of cap greatly diminished
5·00 and 5·25	Large flame spreading through about half the mixture	Size of cap greatly diminished
5·50	Distinct propagation, below the spark, of a blue flame which continued for a short time after the passage of the spark ceased	Small cap above spark about 1·5 cm. high. (A sample of the residual gases in the globe was found to contain about 3 per cent. of methane)
5·70	The flame travelled slowly throughout the mixture	No cap could be seen
5·80 and 5·90	The flame travelled throughout the mixture fairly quickly	No cap could be seen
6·10	The flame travelled rapidly throughout the mixture	No cap could be seen

The lower-limit mixture contains between 5·50 and 5·70 per cent. of methane.

Our results are in good agreement with those obtained by Coquillon and by Mallard and Le Chatelier, but are quite at variance with those obtained by Teclu. The effect of the spark on mixtures containing as much as 4·50 per cent. of methane makes it impossible for us to believe, as Teclu states, that mixtures containing 3·20 or 3·67 per cent. of methane can propagate flame under normal conditions as regards the initial temperature and pressure of the mixtures, and we conclude that either his method of analysis or his method of preparing the mixtures was faulty. In Fig. 3 are given diagrams representing the appearance of the flames in the different mixtures after the first passage of the electric spark, from which it will be seen that no doubt could exist regarding the inability to propagate flame of the mixtures containing a lower percentage of methane than 5·50. These diagrams show the appearance of the flame when it had attained its maximum dimensions.

The manner of movement of the flame in the 5·50 per cent. mixture suggested that if the gases were free to expand, ignition might possibly be propagated for a short distance. To test this, a different form of containing vessel was used, consisting of a vertical glass tube 3·5 cm. in diameter and 180 cm. long. The lower end of this tube expanded into a spherical chamber 10 cm. in diameter, in which platinum electrodes were fixed 20 mm. apart. The upper end of the tube could be closed by a ground-glass stopper.

The gaseous mixture, containing 5·50 per cent. of methane, was passed into the previously evacuated apparatus through a tap near the spherical end. An experiment was first made with the upper end of the tube closed by the glass stopper. On passing the electric spark, the flame of the burning gases filled the spherical chamber and extended about 10 cm. upwards in the vertical tube. A second experiment was then made with a fresh supply of the same mixture. In this experiment, just before the spark was passed, the glass stopper was removed, leaving the upper end of the tube open to the outside air. The flame extended about 30 cm. up the vertical tube, and then died out.

Altogether, we are satisfied that the figure we give, 5·60, represents the smallest possible percentage of methane in a methane and air mixture that can enable self-propagation of flame to take place when the initial temperature and pressure of the mixture are atmospheric.

Ethane.

C_2H_6 present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
2·40	A small flame above the spark, about 3 cm. high	Size of cap slightly diminished
2·70	Flame about 5 cm. high above spark	Size of cap slightly diminished
2·90 and 2·95	Large flame spreading through about one-third of the mixture	Size of cap greatly diminished
3·00	The flame travelled slowly through nearly the whole of the mixture	Small cap above the spark
3·20	The flame travelled fairly quickly throughout the mixture	No cap could be seen
3·35	The flame travelled rapidly throughout the mixture	No cap could be seen
3·50	The movement of the flame throughout the mixture could just be followed with the eye	No cap could be seen

The lower-limit mixture contains between 3·00 and 3·20 per cent. of ethane.

Propane.

C_3H_8 present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
2·00	Small flame above spark about 6 cm. high	Size of cap diminished
2·10	Flame above spark spreading through about one-quarter of the mixture	Size of cap much diminished
2·15	Flame spreading nearly through the whole mixture	Small cap above spark
2·20	The flame spread slowly through the whole mixture	No cap could be seen
2·25	The flame moved fairly quickly through the mixture	No cap could be seen

The lower-limit mixture contains between 2·15 and 2·30 per cent. of propane.

n-*Butane.*

C_4H_{10} present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
1·60	The flame reached the top of the globe and spread sideways through about one-third of the mixture	Small cap above spark
1·70	The flame travelled slowly through the whole mixture; its movement could easily be followed with the eye	No cap could be seen
1·80	The flame travelled fairly quickly through the whole mixture	No cap could be seen

The lower-limit mixture contains between 1·60 and 1·70 per cent. of *n*-butane.

n-*Pentane.*

C_5H_{12} present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
1·25	Flame above spark about 6 cm. high	Size of cap diminished
1·30	Flame above spark spreading through about one-third of the mixture	Size of cap much diminished
1·35	Flame above spark spreading through about half the mixture	Size of cap greatly diminished
1·40	The flame travelled slowly throughout the mixture	No cap could be seen
1·45	The whole of the gas burned fairly quickly	No cap could be seen

The lower-limit mixture contains between 1·35 and 1·40 per cent. of *n*-pentane.

*iso*Pentane.

C_5H_{12} present. Per cent. of mixture.	Effect of momentarily passing spark.	Effect of passing spark a second time.
0·90 and 1·20	Very small cap above spark	——
1·30	Flame above spark spreading through about one-third of the mixture	Small cap above spark
1·35	The flame travelled slowly throughout the mixture	No cap could be seen
1·40 and 1·45	The flame travelled fairly quickly throughout the mixture	No cap could be seen

The lower-limit mixture contains between 1·30 and 1·35 per cent of *iso*pentane.

The Influence of the Size and Intensity of the Initial Source of Heat.—In discussing the influence of the volume of the initial source of heat on the propagation of flame in explosive mixtures of gases, Mallard and Le Chatelier put forward considerations (*loc. cit.*, p. 353), which can be paraphrased as follows: Assume that the source of heat is a sphere the temperature of which is higher than the ignition-temperature of the mixture. Before the molecules actually in contact with this sphere reach ignition-temperature, the surrounding molecules will have attained a certain temperature which will be lower the greater their distance from the heated sphere. The sphere, therefore, must communicate a certain quantity of heat to the surrounding gas before combustion can take place, without losing so much heat as to lower its temperature below the ignition-temperature of the mixture. The amount of heat communicated by the sphere in a given time is proportional to its radius squared (r^2), whilst the total quantity of heat that it contains is proportional to its radius cubed (r^3). It is obvious that the ratio between these two quantities, on which the propagation of inflammation depends, is proportional to the radius, that is to say, to the volume, of the sphere. This is found to be the case in actual experiment; a small electric spark of high temperature is insufficient to cause the inflammation of weak mixtures, which can, however, readily be ignited by the flame of a lamp—of less intensity than the electric spark, but of larger volume.

In the case of non-explosive mixtures, which contain a certain quantity of inflammable gas, but are unable to propagate flame, the introduction of a sphere the temperature of which is maintained above the ignition-temperature of the mixture will cause the combustion of the gas in a zone concentric with the sphere. The heat of combustion will increase the temperature of the surrounding mixture and automatically extend the radius of this zone. The sphere will thus be surrounded by a burning layer, the thickness

which will be greater the higher the temperature of the sphere and the nearer the mixture approaches the lower-limit mixture.

It would appear, therefore, that above a certain limit, no increase in the size and intensity of the source of heat can affect the percentage of combustible gas that must be present to form a lower-limit mixture. The only effect that can follow an increase in the magnitude of the source of heat introduced into a mixture containing less combustible gas than is required to form a lower-limit mixture is an increase in the size of the aureole surrounding it.

We have made a number of experiments with mixtures of methane and air and ethane and air, in which the length of the spark from the induction coil was either 10, 15, 30, or 50 mm. The longest spark was no more effective than the shortest, and no great difference could be observed in the height of the cap formed.

Finally, by employing a Wehnelt electrolytic interrupter in circuit with the primary of the induction coil, using a current of 110 volts, we obtained a "flaming" spark, 30 mm. long, of large volume and great intensity. Comparative experiments were made with this source of ignition with most of the mixtures enumerated in the preceding tables. The results were, in general, as have been anticipated. The percentage of combustible gas required to form a lower-limit mixture suffered no reduction in consequence of the more violent means of ignition, but the size of the aureole surrounding the spark was greatly increased. Moreover, with mixtures that were capable of propagating flame, the flame appeared to travel more rapidly, and a greater pressure was momentarily produced than when the ordinary spark was used to cause ignition.

In illustration of the increase of the size of the aureole, the case of a mixture of ethane and air containing 2·45 per cent. of ethane may be mentioned. With the ordinary spark from the induction coil a cap about 3·5 cm. high appeared above the spark; with the Wehnelt spark the flame of the burning gases reached to the top of the globe and spread outwards through about one-third of the mixture.

The increased rapidity of combustion of inflammable mixtures is well shown in the case of a mixture of ethane and air containing 3·5 per cent. of ethane. When ignited by the ordinary spark the gases burned rapidly, but the movement of the flame could be followed with the eye; ignited by means of the Wehnelt spark, the mixture exploded violently, shattering the globe.

It has been suggested to us that the reason for this increased rapidity of combustion may lie in the great ionising power of the Wehnelt spark, and that, possibly, ionisation from an external source and ignition by means of an ordinary spark might produce

similar effects to the combined ignition and ionisation of the Wehnelt spark. We hope to be able to test this point.

The Influence of Small Variations in the Initial Temperature and Pressure of the Mixtures.—The experiments that we have made on the influence of the initial temperature and pressure of the mixtures in determining their lower-limit values have been confined to such small variations as may occur in coal-mining practise. That is to say, the highest temperatures and pressures that we have employed have been but little more than can exist in the deepest mine at present worked.

Such small variations in temperature and pressure do not appear to have any measurable influence on the lower-limit value of methane and air mixtures. With the initial temperature as high as 35°, and the pressure 800 mm., no self-propagation of flame could be observed with mixtures containing less than 5·60 per cent. of methane. On the other hand, with mixtures of ethane and air there seemed to be a tendency for mixtures containing slightly less than 3·10 per cent. of ethane to propagate flame when the initial pressure of the mixture was greater than 780 mm. and the Wehnelt spark was used; thus, in two experiments a mixture containing 3·00 per cent. of ethane propagated flame, the initial temperature being 24°. In another mixture, containing 2·95 per cent. of ethane, the flame only travelled through about two-thirds of the mixture.

We hope to be able to extend this work to a more complete study of the effect of pressure on the lower limit.

We wish to express our thanks to the Mining Association of Great Britain for permission to publish these results; and to the Explosions in Mines Committee of the Home Office for ratifying that permission.

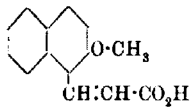
ALTOFTS.

CCXXIX.—*β-2-Methoxynaphthylpropionic Acid and Methoxy*peri*naphth-hydrindone.*

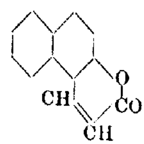
By GEORGE BARGER and WALTER WILLIAM STARLING.

A RECENT paper by Sachs and Brigl (*Ber.*, 1911, **44**, 2091) on ring-formation in the *peri*-position in the naphthalene series induces us to publish some experiments on the same subject which we made about a year ago, with but partial success. The method we wished to adopt was very similar to that which Sachs and Brigl had in view, namely, the removal of water from a naphthylacrylic or

ropionic acid by a reaction like that used in the preparation of ydrindone. In order to prevent ring-formation by the removal the hydrogen atom in position 2, we first replaced that hydrogen tom by a methoxy-group, and started therefore from 2-methoxy-aphthaldehyde. This was fairly readily converted into 2-methoxy-aphthylacrylic acid (I):

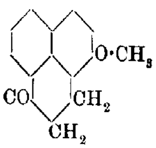


(I.)



(II.)

Sachs and Brigl, who employed the corresponding ethoxyaldehyde, ere unable to bring about a similar condensation, and only btained naphthacoumarin (II) by loss of the ethyl group. In our se this difficulty made itself felt in the next reaction (with phos-horic oxide), so that we likewise failed in our attempt to form a rinaphthindenone. When the naphthylacrylic acid was heated ith excess of phosphoric oxide in benzene solution, no product ould be isolated except a little of the naphthacoumarin (II), and his substance was also formed, in much larger quantity, when we eated the acrylic acid with one molecular proportion of phosphorus entachloride. On the other hand, when we had reduced the aphthylacrylic acid to the corresponding propionic acid, its ehaviour towards phosphoric oxide was changed, and we obtained small quantity of a substance which we consider to be a rinaphth-hydrindone of the constitution III:



(III.)

The yields of methoxynaphthylpropionic acid and also of the bove substance were so small that we were unable to prepare the orresponding phenol in order to submit it to distillation with inc dust, as we had hoped to do.

Experimental.

Methylation of 2-Hydroxynaphthaldehyde.

Commercial hydroxynaphthaldehyde (from Schuchardt) and methyl sulphate were used. To 50 grams of the aldehyde, dissolved

in 440 c.c. of methyl alcohol, were added 28·6 c.c. of methyl sulphate, and then 27·4 c.c. of aqueous potassium hydroxide (11*N*). The addition of methyl sulphate and of potassium hydroxide was repeated twice. Each time a vigorous reaction should take place, and large quantities give a better yield than smaller ones. In the above experiment 43 grams of ether were obtained, and 10 grams of the hydroxyaldehyde were recovered. These were again methylated, so that the final yield amounted to 95 per cent. of the theory.

2-Methoxynaphthaldehyde is best purified by distillation; it boils at 205°/18 mm., and melts at 84°.

β-2-Methoxynaphthylacrylic Acid, $CH_3{\cdot}O{\cdot}C_{10}H_6{\cdot}CH{:}CH{\cdot}CO_2H$.

The above aldehyde did not react with sodium acetate and acetic anhydride, but it did with ethyl acetate and sodium. Ten grams of the aldehyde dissolved in 9·5 grams of ethyl acetate were treated with 1·25 grams of finely divided sodium (prepared by shaking under hot toluene). The resulting ester was hydrolysed on the water-bath with methyl-alcoholic sodium hydroxide, and yielded 11 grams of the crude acid, which separated from benzene and light petroleum in very pale yellow needles, melting at 160°:

0·1580 gave 0·4261 CO_2 and 0·0765 H_2O. C = 73·55; H = 5·4.

0·1286 was neutralised by 5·6 c.c. *N*/10-NaOH. M.W. = 229.

$C_{14}H_{12}O_3$ requires C = 73·7; H = 5·3 per cent.; M.W. = 228.

When the acid was heated on the water-bath in benzene solution with phosphoric oxide we could only isolate a minute quantity of a yellow, crystalline, neutral substance, which could not be purified completely, but was probably naphthacoumarin, first prepared by Kaufmann (*Ber.*, 1883, **16**, 686). The melting point was very indefinite, at about 80°, instead of 118°. By heating the same acid with one molecular proportion of phosphorus pentachloride on the water-bath, and distilling under diminished pressure, we obtained a 65 per cent. yield of a yellow substance, boiling at about 240°/12 mm. After crystallisation from benzene and light petroleum it melted at 117°, and was further identified with naphthacoumarin by analysis (Found, C = 79·8; H = 4·2. Calc., C = 79·6; H = 4·1 per cent.), and by the green fluorescence of its solution in concentrated sulphuric acid.

It is clear, therefore, that the methyl group was eliminated in the same way as the ethyl group in the experiments of Sachs and Brigl. The saturated acid, however, was found to react somewhat differently with phosphoric oxide, and in this case we obtained the desired *peri*naphth-hydrindone.

β-2-Methoxynaphthylpropionic Acid, $CH_3\cdot O\cdot C_{10}H_6\cdot CH_2\cdot CH_2\cdot CO_2H$.

The crude methoxynaphthylacrylic acid obtained from 20 grams of the aldehyde was reduced in sodium carbonate solution by 1 kilo. of 3 per cent. sodium amalgam, the solution being stirred by a motor. The mixture of acids which resulted was precipitated by hydrochloric acid, and extracted with several litres of boiling water, from which the saturated acid separated on cooling in colourless needles, melting at 128°. Yield, 2·6 grams:

0·2596 gave 0·6981 CO_2 and 0·1439 H_2O. C=73·3; H=6·1.

0·1500 was neutralised by 6·45 c.c. N/10-KOH. M.W.=232.

$C_{14}H_{14}O_3$ requires C=73·0; H=6·1 per cent.; M.W.=230.

The acid did not reduce potassium permanganate. It dissolved in about 1000 parts of boiling water.

*Methoxy*peri*naphth-hydrindone*, $C_{14}H_{12}O_2$.

With the small quantity of the last-named acid at our disposal we could only carry out a few experiments with phosphoric oxide. The most successful one was as follows: 1·3 grams of the acid were dissolved in 10 c.c. of benzene, and heated on the water-bath with 6·7 grams of phosphoric oxide for two to three hours. Powdered ice was then added to the reddish-violet reaction product, and after extraction with ether and washing with sodium carbonate, we obtained a small quantity of a yellow substance, which was distilled at 210°/12 mm., and then crystallised from benzene and light petroleum in deep yellow prisms, melting at 135°:

0·1314 gave 0·3897 CO_2 and 0·0583 H_2O. C=79·1; H=4·8.

$C_{14}H_{12}O_2$ requires C=79·2; H=5·6.

$C_{14}H_{10}O_2$ „ C=80·0; H=4·8 per cent.

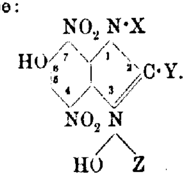
Of these two formulæ the first is by far the most likely. We satisfied ourselves that the methoxy-group was still intact, for on boiling with hydriodic acid, methyl iodide was evolved, but we had not enough material to repeat the analysis. We hope to find a better method of reducing methoxynaphthylacrylic acid in order to continue the experiments.

CHEMICAL LABORATORY, GOLDSMITHS' COLLEGE,
NEW CROSS, LONDON, S.E.

CCXX.—*Syntheses with Phenol Derivatives Containing a Mobile Nitro-group. Part V. Quinone-imides, Asymmetric Quaternary Ammonium Compounds, and Asymmetric Carbinols (continued).*

By RAPHAEL MELDOLA and HAROLD KUNTZEN.

THE main object of the present extension of the research has been the study of the influence of the radicles X, Y, and Z in iminazolium compounds of the type:



on the general properties of these compounds, with a view to the selection of the most suitable types for the proposed investigation of the optical properties in the event of the bases or carbinols being resolvable. It was pointed out in our last paper (this vol., p. 1283) that the radicles in question were completely under control, and in the cases hitherto studied X has stood for phenyl and *p*-tolyl, and Z, excepting in one case, for methyl. In the present paper we describe other sets of compounds, in which X is represented by *p*-chlorophenyl, *p*-anisyl, and benzyl, Y and Z standing for methyl. Special attention has also been paid to the radicle Y attached to the 2-carbon atom, with a view to obtaining a series of homologues, and we have succeeded in preparing the compounds in which Y is represented by ethyl and *iso*butyl respectively, Z standing throughout this series for methyl, and X for phenyl. It is evident that there is scope for the indefinite extension of the research in the direction of synthesising new iminazoles and carbinols, but the fertility of the method has been sufficiently proved by the cases studied in this and the former papers, and it will be unnecessary to multiply instances, except for the elucidation of special points of theoretical interest. The general outcome of the experiments up to this point is to show that when the radicle X contains an acid substituent (Cl), the ammonium base forms salts of greater stability than when no such substituent is present. It appears also that with increase of weight in Y the general internal mobility also increases, so that in the higher homologues the conversion of the carbinol into the ammonium base takes place with extreme facility, a fact which

may be taken as proving that in this series the presence of hydroxyl in the benzene ring so influences the character of the molecule as to render the quinoneimide form the more stable. In this connexion it is of interest to recall the observations of Japp and Moir (Trans., 1900, **77**, 608), which indicate that in the case of the derivatives of lophine the carbinol form is the more stable, since the ammonium form passes readily into the latter.*

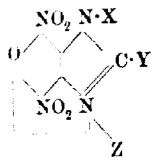
Further Theoretical Considerations.

The extension of the work since our last communication has led incidentally to the reconsideration of the theoretical interpretation of our results, and certain questions of considerable importance in relation to the formulæ proposed have necessarily arisen. As the result of our later work we see no reason for modifying the views advanced in our last paper, although there are certain assumptions upon which these views rest which require further verification. We propose calling attention to some of these points now, as much evidence will have to be accumulated before the questions raised can be satisfactorily settled. The question as to which of the two forms is the carbinol has already been dealt with (this vol., p. 1285). The evidence, as far as it goes, seems fairly conclusive, although the basic character of the isomeric iminazolium compound as evidence of the constitution of that form is to some extent weakened by the circumstance that the carbinols obtained by Otto Fischer are also basic (*J. pr. Chem.*, 1906, [ii], **73**, 422). It does not appear, however, from the researches of this author that the carbinols containing acid substituents in the benzene ring are likewise basic.

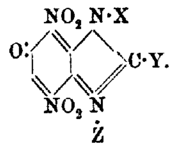
The argument from colour, although, as already pointed out (*loc. cit.*, p. 1286), subject to limitations, is, as far as it goes, in favour of the "quinoneimide" structure of the highly-coloured red form. The formula suggested for this modification on the strength of the evidence from colour, together with the chemical evidence already submitted, confessedly raises a difficulty which has led to the consideration of other possible formulæ for these coloured compounds. The formula in question (I) represents the quinonoid character, the relationship to the ammonium base, and the basic property of the molecule (see the general scheme in the last paper, *loc. cit.*, p. 1287), all of which characters are possessed by these red compounds. On the other hand, the alternative quinonoid formula (II) necessitates the assumption that a quinquevalent nitrogen atom

* The work of these authors furnishes a good example of the opening out of the iminazole ring, the ammonium hydroxide form of an amarine derivative passin spontaneously into the ethylenediamine derivatives.

can be in direct combination with carbon only, a state of combination hitherto unknown among quinquevalent nitrogen compounds. In answer to this objection it might be urged that the compounds

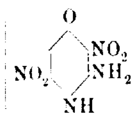


(I.)

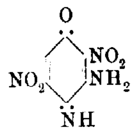


(II.)

are capable of existing in form I only, and not in the tautomeric form II. In other words, they may be regarded as derivatives of the hypothetical dinitroaminoquinoneimide (III), and not of its tautomeride (IV):



(III.)



(IV.)

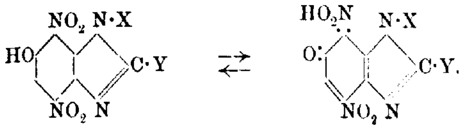
Formula I represents the compound as the inner anhydride of the ammonium hydroxide derivative, and is in harmony with the fact that in some cases the transformation has been followed quantitatively by determining the actual loss of water on drying.* This formula does not violate any of the recognised canons of the constitution of the quinquevalent nitrogen compounds, as the fifth nitrogen bond is combined with the substituted acid phenyl nucleus. By this discussion there is thus raised the question of the possible existence of fixed quinonoid constitution, that is, of quinonoid compounds incapable of assuming the tautomeric (Fittig) form.

With respect to the possibility of quinquevalent nitrogen having all its bonds attached to carbon, it may be pointed out that groupings of the type $:C{=}\dot{N}{=}C:$, in which both carbon atoms are contained in ring systems, have not hitherto been obtained so far as we are aware, so that no evidence from analogy appears to be available. In our compounds it will be noticed that one of the carbon atoms belongs to a ring highly charged with negative substituents, and may therefore be regarded as belonging to an *acid*

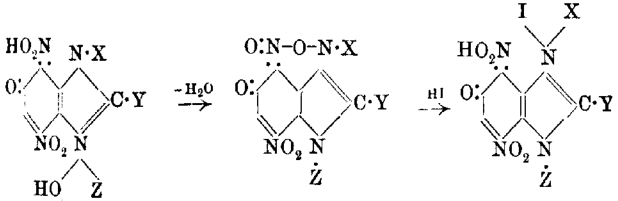
* It is only right to point out that in the majority of cases hitherto studied the ammonium hydroxide form could not be isolated, as it loses water readily, even on exposure to the air at the ordinary temperature, and passes into the anhydro-form. The extreme stability of these compounds when heated with concentrated sulphuric acid to the fuming point (this vol., p. 1294) is connected with the fact that it is the iminazolium sulphate which is being dealt with under these conditions.

radicle. From this point of view the proposed formula falls into line with compounds of the oxy-trialkylamine type.

Of other possible formulæ, that which represents the coloured compounds as having an ortho-quinonoid structure has received much consideration. The researches which have been carried out by Hantzsch and his colleagues during the few past years have made us familiar with the existence of the *iso*nitro-group (NO_2H) in compounds which had formerly been regarded as true nitro-derivatives, and reasons have already been given for suspecting such tautomerism in the original trinitroacetylaminophenol from which our iminazoles are prepared (Trans., 1910, **97**, 453). It is, in fact, possible, although we have no direct evidence to adduce in support of such a view, that the iminazoles themselves may be susceptible of such tautomerism:



In this connexion it is perhaps worth recalling attention to the fact that all our iminazoles are in the solid state or in solution of a pale ochreous colour, while their alkaline solutions and their solid salts are of an orange colour. Assuming, therefore, in accordance with the generally accepted view (Pinnow and Sämann, *Ber.*, 1899, **32**, 2181; Japp and Moir, Trans., 1900, **77**, 614) that when in a ring system an atom of nitrogen becomes quinquevalent, it is preferentially that atom which is associated with the double linking, the methiodide and corresponding ammonium base might be formulated on the above hypothesis as quinonoid compounds (I), anhydridisation taking place with rearrangement of internal linking between the 3-hydroxyl group and the 7-*iso*nitro-group. The product would then be an "inner" salt of the nitroic acid type, and would have an ortho-quinonoid structure (II):

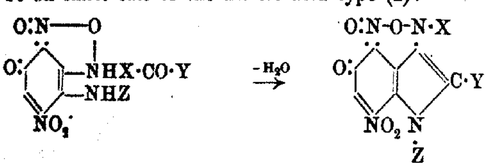


(I.) (II.) (III.)

This hypothesis is certainly worthy of being kept in view, although the balance of evidence seems to us to be against it. Some

of the objections to the proposed alternative scheme are worthy of record in view of their being met by further experimental evidence. In the first place, anhydridisation between hydroxyl groups in the meta-position is less probable than between such groups in the para-position, as is assumed in our original hypothesis. In the next place the formation of salts (iodides) by combining the quinonoid compounds (II) with acids would lead to the production of compounds isomeric with the original methiodide (III), unless we assume that there is another rearrangement of internal linking and the reconversion of the 3*N*-atom into the quinquevalent form. This is, of course, a possibility, but it introduces unnecessary complication into the chemical mechanism, and, as a fact, no such isomerism has hitherto been observed, the iodide obtained by combining the quinoneimide with hydriodic acid being apparently identical with the methiodide obtained by direct methylation of the iminazole (this vol., p. 1296).

The objection to the supposition that anhydridisation can take place between hydroxyl groups in the meta-position might perhaps be met by assuming that the hydrolysis of the methiodide results in the opening out of the iminazole ring with the formation of an intermediate ortho-diamine derivative, which, on this supposition, would be an inner salt of the nitroic acid type (I):



(I.) (II.)

The latter might then be supposed to anhydridise in the usual way with the formation of the ortho-quinonoid compound (II). This view, which, as we learn from a private communication, has also suggested itself to Dr. James Moir, is, however, at variance with the experimental evidence. In no case have we observed any tendency for the iminazole ring to break down in our compounds, and experiments directed specially towards this end have, as shown in our last paper, thus far led to negative results. If the iminazole ring in these compounds were so easily broken down, they might be expected, in accordance with Otto Fischer's results, to furnish nitrosoamines by the action of nitrous acid, azines by oxidation, and ortho-diamine derivatives by complete hydrolysis. No one of these properties is possessed by our compounds. A crucial test of the validity of the ortho-quinonoid formula would be the formation of analogous compounds containing some substituent other

than a nitro-group in position 7. Experiments having for their object the synthesis of iminazoles containing a halogen atom in this position have been commenced, but we have not yet succeeded in preparing compounds of this type; this branch of the work has, however, only been tentatively dealt with at present.

So far as concerns the formation of the carbinol from the ammonium compound, either the ortho- or the para-quinonoid formula will represent the transformation. The balance of evidence is, however, thus far so distinctly in favour of the latter that we see no reason for departing from our original view of the constitution of these compounds.

Experimental.

In order to condense the descriptive details of the work as much as possible, each set of compounds is dealt with under the heading indicating the iminazole used as the starting point. In all cases the methiodide was first prepared.

The Iminazole from Trinitroacetylaminophenol and p-*Anisidine.*

The iminazole (Meldola and Hay, Trans., 1908, **93**, 1675) was converted into the iminazolium iodide by heating with excess of methyl iodide for three hours at 125°. The iodide, which consists of small, ochreous needles, is slowly decomposed by boiling with water, but more rapidly by boiling with dilute hydrochloric acid. On neutralising the hot acid solution with ammonia, the iminazolium compound separates out on cooling as a brick-red, microcrystalline powder. The air-dried substance proved on analysis to be the quinoneimide, 4:7-*dinitro*-1-p-*anisyl*-2:3-*dimethyl*-6-*benziminazolone*, a fact indicating that anhydridisation takes place very readily in this case, possibly in the hot aqueous solution:

0·0986 gave 13·7 c.c. N_2 (moist) at 21·5° and 759·9 mm. N = 15·77.

$C_{16}H_{14}O_6N_4$ requires N = 15·66 per cent.

The substance is extremely basic, dissolving readily in dilute acids with the formation of salts which are stable only in presence of excess of acid. The hydrochloride (4:7-*dinitro*-6-*hydroxy*-1-p-*anisyl*-2:3-*dimethylbenziminazolium chloride*) was prepared by the action of a saturated alcoholic solution of hydrogen chloride on the foregoing compound. It consists of small, white needles, easily dissociable by water:

0·0968 gave 0·0351 AgCl. Cl = 8·96.

0·0858 „ 10·5 c.c. N_2 (moist) at 21·5° and 763 mm. N = 13·95.

$C_{16}H_{15}O_6N_4Cl$ requires Cl = 8·98; N = 14·2 per cent.

The carbinol, *4 : 7-dinitro-6-hydroxy-1-p-anisyl-2 : 3-dimethyl-2-benziminazolol*, was prepared by dissolving the iminazolone in warm dilute sodium hydroxide, and precipitating by hydrochloric acid. The compound separates as a microcrystalline, ochreous powder, which passes readily into the red iminazolone on heating, the conversion taking place in a few minutes on boiling with alcohol or water, and also slowly on drying the solid at 100°. The best analytical results were for this reason given by the air-dried substance:

0·1016 gave 13·2 c.c. N_2 (moist) at 19° and 771·5 mm. N = 15·17.

$C_{16}H_{16}O_7N_4$ requires N = 14·89 per cent.

The Iminazole from Trinitroacetylaminophenyl and p-*Chloroaniline.*

The iminazole (m. p. 246°; Meldola and Hay, Trans., 1908, **93**, 1676) had to be heated with excess of methyl iodide to 130° for two to three hours to bring about complete transformation into the methiodide. The latter is a crystalline substance, consisting of dark ochreous scales. Decomposition was effected by boiling with dilute hydrochloric acid, the iminazolone being precipitated from the acid solution on adding ammonia in slight excess. This compound crystallises in small, ochreous scales, which do not decompose at 300°. An air-dried specimen was used for analysis:

0·0832 gave 11·5 c.c. N_2 (moist) at 20° and 759·5 mm. N = 15·8.
0·1088 ,, 0·0420 AgCl. Cl = 9·54.

$C_{15}H_{11}O_5N_4Cl$ requires N = 15·45; Cl = 9·77 per cent.

This compound (*4 : 7-dinitro-1-p-chlorophenyl-2 : 3-dimethyl-6-benziminazolone*) is characterised by the stability of its hydrochloride, which is not completely dissociated by excess of hot water. It is for this reason that excess of ammonia is required for the precipitation of the pure iminazolone from its acid solution. The salt (*4 : 7-dinitro-6-hydroxy-1-p-chlorophenyl-2 : 3-dimethylbenziminazolium chloride*) was prepared by dissolving the iminazolone in hot 50 per cent. hydrochloric acid, filtering, and allowing to cool, when the compound separated as a white, microcrystalline powder, which was collected, washed with a little cold water, and allowed to dry in the air:

0·2012 gave 24·4 c.c. N_2 (moist) at 17° and 761·5 mm. N = 14·16.
0·1627 ,, (on decomposition by an alcoholic solution of silver nitrate) 0·0572 AgCl. Cl = 8·70.

$C_{15}H_{12}O_5N_4Cl_2$ requires N = 14·04; Cl (1 atom) = 8·88 per cent.

The carbinol, *4 : 7-dinitro-6-hydroxy-1-p-chlorophenyl-2 : 3-dimethyl-2-benziminazolol*, was prepared in the usual way by dissolving the iminazolone in alkali, and precipitating by acid. It consists of an

ochreous, non-basic, microcrystalline powder, which is converted into the basic iminazolone on boiling with alcohol or water:

0·0976 gave 12·8 c.c. N_2 (moist) at 21° and 760·1 mm. N = 14·93.
$C_{15}H_{13}O_6N_4Cl$ requires N = 14·72 per cent.

It will be noted that in this case, as in that of the *p*-tolyl compound (this vol., p. 1286), the iminazolone and carbinol do not differ markedly in colour.

The Iminazole from Trinitropropionylaminophenol and Aniline.

After numerous experiments having for their object the preparation of iminazoles having radicles other than methyl attached to the 2-carbon atom, it was found that the most satisfactory results were obtained by acylating the trinitroaminophenol prepared by the hydrolysis of its acetyl derivative (Meldola and Hay, Trans., 1909, **95**, 1378). For the present series the dry trinitroaminophenol was heated for some time on the water-bath with excess of propionic anhydride, the product diluted with water, and the solid propionyl compound purified by crystallisation from glacial acetic acid.

2:3:5-*Trinitro-4-propionylaminophenol* crystallises from acetic acid in nodular aggregates of opaque, ochreous needles, melting at 178—179°:

0·0915 gave 15·1 c.c. N_2 (moist) at 21·5° and 760·7 mm. N = 18·76.
$C_9H_8O_8N_4$ requires N = 18·67 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-ethylbenziminazole* was prepared from the above trinitro-compound by boiling it in alcoholic solution with aniline according to the method described in former papers. The product after crystallisation from alcohol with the addition of animal charcoal was obtained in ochreous, transparent, rhombohedral plates, becoming opaque at 100°, and melting at 173°:

0·1666 gave 24·5 c.c. N_2 (moist) at 17·5° and 760·7 mm. N = 17·04.
$C_{15}H_{12}O_5N_4$ requires N = 17·08 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-ethyl-3-methylbenziminazolium iodide* was prepared by heating the iminazole with excess of methyl iodide to 120° for three hours. The product consisted of small, reddish-brown scales, the analysis of which indicated that the formation of the methiodide was practically complete:

0·1814 gave 18·3 c.c. N_2 (moist) at 18·7° and 755·7 mm. N = 11·54.
$C_{16}H_{15}O_5N_4I$ requires N = 11·92 per cent.

4:7-*Dinitro-1-phenyl-3-methyl-2-ethyl-6-benziminazolone* was obtained from the iminazolium iodide by boiling the latter with dilute hydrochloric acid, and neutralising the filtrate with ammonia. After

being twice treated in this way, the pure compound was obtained in small, brick-red scales, decomposing above 300°:

0·0978 gave 13·9 c.c. N_2 (moist) at 21·5° and 774·4 mm. N=16·[illegible].

$C_{16}H_{14}O_5N_4$ requires N=16·47 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-ethyl-3-methylbenziminazolium chloride* was prepared from the iminazolone by treating the latter in the cold with an alcoholic solution of hydrogen chloride. It crystallises in white granules, easily dissociable by water:

0·1500 gave 19·3 c.c. N_2 (moist) at 23° and 772 mm. N=14·66.
0·2258 „ 0·0829 AgCl. Cl=9·08.

$C_{16}H_{15}O_5N_4Cl$ requires N=14·8; Cl=9·36 per cent.

The carbinol, 4:7-*dinitro-6-hydroxy-1-phenyl-3-methyl-2-ethyl-2-benziminazolol*, was prepared in the usual way by the action of dilute sodium hydroxide on the iminazolone, and precipitation by acid. It crystallises in microscopic, ochreous needles, which pass very readily into the red iminazolone on boiling with water or alcohol or on heating in the dry state:

0·0833 gave 0·1632 CO_2 and 0·0326 H_2O. C=53·43; H=4·35.
0·0786 „ 11·1 c.c. N_2 (moist) at 25° and 764·6 mm. N=15·55.

$C_{16}H_{16}O_6N_4$ requires C=53·3; H=4·48; N=15·55 per cent.

*The Iminazole from Trinitro*iso*valerylaminophenol and Aniline.*

Attempts to prepare trinitro*iso*valerylaminophenyl by first introducing one or two valeryl groups into *p*-aminophenol and then nitrating the product under various conditions, showed that this method was unsatisfactory. The divaleryl compound is easily prepared by the action of valeric anhydride on *p*-aminophenol in the presence of a few drops of sulphuric acid, but the product is viscous and uncrystallisable. It can be nitrated in cooled glacial acetic acid by means of fuming nitric acid, and yields a *dinitro*-derivative, which crystallises in flat, ochreous needles, melting at 177°. The *O*-valeryl group is eliminated during nitration as the product is phenolic, and has the composition of a *dinitromonovaleryl*-p-*aminophenol*:

0·1186 gave 15·05 c.c. N_2 (moist) at 14° and 768·2 mm. N=15·09.

$C_{11}H_{13}O_6N_3$ requires N=14·84 per cent.

This dinitro-compound could not be readily converted into a trinitro-compound, so the method was abandoned, and the alternative process of acylating trinitroaminophenol adopted.

2:3:5-*Trinitro-1:4-di*iso*valerylaminophenol* was prepared by the action of excess of *iso*valeric anhydride on *p*-aminophenol. In the presence of sulphuric acid acylation takes place readily at the

dinary temperature in the course of a few hours; without lphuric acid acylation takes place readily on warming on the ater-bath for about an hour. In both cases the divaleryl mpound is produced, the latter crystallising from alcohol in pale llow needles, melting at 119°:

0·0770 gave 9 c.c. N_2 (moist) at 16° and 762·7 mm. N = 13·68.

$C_{16}H_{20}O_9N_4$ requires N = 13·59 per cent.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-*iso*butylbenziminazole* was preared by heating the foregoing compound with excess of aniline in coholic solution in the usual way. After purification by alkaline eatment and crystallisation from alcohol, it consists of ochreous ales, melting at 156°:

0·1712 gave 0·3602 CO_2 and 0·0778 H_2O. C = 57·39; H = 5·04.

0·1330 „ 18·2 c.c. N_2 (moist) at 20° and 759·4 mm. N = 15·63.

$C_{17}H_{16}O_5N_4$ requires C = 57·27; H = 4·52; N = 15·73 per cent.

It is of interest to note that during the formation of this iminle, the *O-iso*valeryl group is eliminated, and that *iso*valeranilide found among the products left after the process of purification y alkaline extraction.

4:7-*Dinitro-6-hydroxy-1-phenyl-2-*iso*butyl-3-methylbenziminzolium iodide* was prepared by heating the iminazole in a sealed ube with excess of methyl iodide for three hours at 120°. The ethylation appeared to be very complete, the methiodide crystalsing in orange-red needles. Decomposition of the methiodide was eadily effected by boiling the crystalline compound with dilute ydrochloric acid, in which it freely dissolves, filtering the solution, nd neutralising with ammonia, when the iminazolium base is recipitated as an orange, microcrystalline powder. In order to nsure complete decomposition of the methiodide, the treatment ith dilute hydrochloric acid was repeated.

4:7-*Dinitro-1-phenyl-3-methyl-2-*iso*butyl-6-benziminazolone* is a ubstance of distinctly basic character, dissolving readily in all ineral acids, and being precipitated unchanged on neutralising he acid solution with ammonia. The decomposing point is above 00°. The compound may exist in the ammonium hydroxide form hen freshly precipitated, but it loses water on drying in the air t the ordinary temperature, and passes into the quinoneimide:

0·1148 gave 15·5 c.c. N_2 (moist) at 22° and 772·6 mm. N = 15·55.

$C_{18}H_{18}O_5N_4$ requires N = 15·13 per cent.

The *iminazolium chloride* is formed from the quinoneimide by he action of an alcoholic solution of hydrogen chloride, from which olvent it separates in small, white needles, readily dissociable by ater with the regeneration of the quinoneimide:

0·1286, decomposed in alcoholic solution with silver nitrate, gave 0·0455 AgCl. Cl = 8·74.

$C_{18}H_{19}O_5N_4Cl$ requires Cl = 8·71 per cent.

The carbinol, 4 : *7-dinitro-6-hydroxy-1-phenyl-3-methyl-2-isobutyl-2-benziminazolol*, was prepared in the usual way by dissolving the quinoneimide in warm dilute sodium hydroxide, and precipitating by hydrochloric acid. It crystallises in small, ochreous needles, which pass with extreme readiness into the ammonium form, a few minutes' boiling with water or alcohol being sufficient to convert the phenolic carbinol into the basic ammonium compound. The specimen used for analysis was dried in the air at the ordinary temperature, as heating in the water-oven brings about partial dehydration owing to the formation of the quinoneimide:

0·1263 gave 16·3 c.c. N_2 (moist) at 22·5° and 757·2 mm. N = 14·52.
0·1182 „ 0·2404 CO_2 and 0·0522 H_2O. C = 55·47; H = 4·91.
$C_{18}H_{20}O_6N_4$ requires C = 55·64; H = 5·19; N = 14·43 per cent.

The Iminazole from Trinitroacetylaminophenol and Benzylamine.

The iminazole (Trans., 1906, **89**, 1940) was methylated by heating with excess of methyl iodide for two hours at 120°. The methiodide consisted of red, ochreous scales, which required prolonged boiling with water in order to effect conversion into the iminazolium compound, the latter crystallising from the solution on cooling in bright red needles, melting and decomposing at 252—253°. Analyses of the air-dried substance showed that dehydration had taken place with the formation of the iminazolone, 4 : *7-dinitro-1-benzyl-2 : 3-dimethyl-6-benziminazolone*:

0·0638 gave 8·9 c.c. N_2 (moist) at 12·5° and 751·3 mm. N = 16·33.
$C_{16}H_{14}O_5N_4$ requires N = 16·37 per cent.

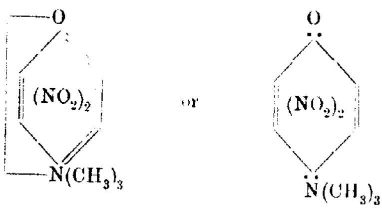
The *iminazolium chloride* was prepared by dissolving the iminazolone in alcoholic hydrochloric acid and adding ether; the salt separates as a pale, ochreous, microcrystalline powder, having when dry a melting point of 218°:

0·0638 gave 8·1 c.c. N_2 (moist) at 14° and 764·5 mm. N = 15·02.
0·1328 „ (by the method of Carius) 0·0501 AgCl. Cl = 9·32.
$C_{16}H_{15}O_5N_4Cl$ requires N = 14·8; Cl = 9·36 per cent.

The salt used for analysis was air-dried, as it dissociates on heating, and also rapidly in contact with water, the red iminazolone being regenerated. We have been unable to prepare the carbinol form of this compound owing to the extreme difficulty of realising the precise conditions necessary in order to ensure successful conversion of the iminazole into the iminazolium iodide. Numerous

experiments have been made under various conditions, but the results have so far been unsatisfactory. As the completion of this series is not of immediate importance, this part of the research has for the present been abandoned.

We desire, in concluding, to express our indebtedness to the Government Grant Fund of the Royal Society for material assistance towards the expenses of the research. We have also much pleasure in acknowledging the valuable co-operation of Mr. William F. Hollely, who has taken a considerable part in the experimental work. We may point out also that while the foregoing results were being prepared for publication, another research being carried out in our laboratory has led to the unexpected discovery of independent confirmation of the existence of quinoneimidonium compounds of the type:



in which quinquevalent nitrogen is combined with three alkyl groups and a carbon atom belonging to the strongly acid quinonoid radicle $[C_6H_2(NO_2)_2O]^{II \text{ or } IV}$, and therefore ascribable to the type of the oxytrialkyl or mixed ammonium compounds, $O\colon N(Alk)_3$, $O\colon N(Alk)_2Ar$, etc. This discovery has arisen from the further study of the product of the extreme methylation of *iso*picramic acid described in a preliminary note by one of the authors published last year (Proc., 1910, **26**, 232). This research is in progress, and the results will be communicated to the Society when sufficiently mature.

City and Guilds of London Technical College,
Finsbury.

CCXXXI.—*The Synthesis of Derivatives of Thioxanthone. Part IV. Synthesis from Aromatic Sulphinic Acids.*

By Harold Christopher and Samuel Smiles.

In previous communications it has been shown that various types of thioxanthone derivatives may be synthesised from aromatic mercaptans (Trans., 1910, **97**, 1290), from aromatic disulphides (this vol., p. 1353), and from the products obtained by the union of a quinone with *o*-thiolbenzoic acid (this vol., p. 1535). In the two former methods the union of the thio-derivative with the aromatic compound is effected by the condensation of a sulphoxylic acid which is formed at an intermediate stage in the process, water being eliminated from this substance and the second aromatic nucleus. Since it has been formerly observed (Smiles and Le Rossignol, Trans., 1906, **89**, 700) that aromatic sulphinic acids readily condense with suitable aromatic compounds in the presence of sulphuric acid:

$$Ar \cdot SO_2H + HAr' = ArSOAr' + H_2O,$$

the present experiments were undertaken in order to apply this type of interaction to the production of thioxanthones.

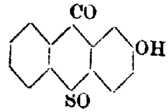
Both Graebe (*Annalen*, 1891, **263**, 1) and Mayer (*Ber.*, 1909, **42**, 1134, 3046) have shown how easily thioxanthones are formed by elimination of water from the *o*-carboxylic derivatives of substituted diphenyl sulphides:

$$C_6H_4{<}^{CO_2H}_{S}{-\!\!-}C_6H_5 = H_2O + C_6H_4{<}^{CO}_{S}{>}C_6H_4,$$

so that the synthesis of thioxanthones by this method is merely a question of choosing suitable aromatic derivatives for condensation with the sulphinic acid. This condensation takes place most readily with hydroxy- and amino-derivatives of benzene, and, since the quadrivalent sulphur grouping then enters the para-position (Smiles and Le Rossignol, *loc. cit.*) with respect to these groups, the *m*-hydroxy- and amino-benzoic acids have been employed in these experiments.

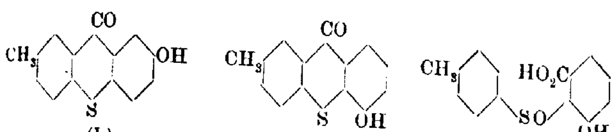
Two methods of effecting the condensation have been investigated, either with warm sulphuric acid or by the aid of heat alone (see Hinsberg, *Ber.*, 1903, **36**, 107); but since the former agent furnishes very poor yields, the latter has been generally adopted. It might be expected that the product furnished by either process would

not be the thioxanthone, but instead the oxide thereof, for example,



but this is not the case, for it appears that at the relatively high temperatures employed the sulphoxide is easily reduced to the sulphide at the expense of the sulphinic acid. In order to obtain the maximum yields of the thioxanthone, it is therefore necessary to employ an excess of sulphinic acid beyond that required by theory, and since even then the yields are not good, the method cannot be recommended for the preparation of the thioxanthones in large quantities.

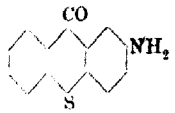
Setting out from a sulphinic acid of known constitution, it is evident that the structure to be assigned to the resulting thioxanthone must be chosen from two alternative formulæ which differ in the position taken by the sulphur with respect to the hydroxy- or amino-groups. The alternatives may be illustrated with the case of the condensation of *p*-toluenesulphinic acid with *m*-hydroxybenzoic acid:



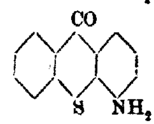
(I.) (II.) (III.)

From the general results obtained in studying the influences which govern the sulphination of hydroxy-derivatives of benzene, the second type of alternative (II) cannot be entertained as highly probable, for it has been shown that the course of this reaction is susceptible to the influence of "steric" conditions; thus, in forming a substance of type II, not only must ortho-condensation occur in preference to the more general para-condensation, but in forming the parental carboxylic acid (III) it must take place under the more adverse steric conditions. For these reasons we consider that preference must be given to the first type of formula (I), which involves the para-condensation, and the contention is supported in the case of the aminothioxanthone furnished by benzenesulphinic acid and *m*-aminobenzoic acid. The substances possessing the alternative structures in question, 2- and 4-aminothioxanthones (IV and V), have been prepared by F. Mayer (*Ber.*, 1909, **42**, 3046) with methods which leave no room for doubt as to the constitution of the products. These substances melt respectively at 222° and

203°, whilst that obtained by ourselves melts at the temperature ascribed to the first-named isomeride. We take this opportunity



(IV).



(V.)

of expressing our thanks to Dr. Mayer for kindly placing at our disposal a small quantity of the 2-amino-derivative. A close comparison of this substance with that obtained by ourselves finally proved the identity of the latter.

Since there is no reason to suspect that the *o*- and *p*-toluenesulphinic acids should behave differently from benzenesulphinic acid, a corresponding structure has been assigned to other amino- and hydroxy-derivatives of thioxanthone which have been prepared from those substances.

It is evident that the method of synthesis now described may be further varied by changing the situation of the carboxyl group in the components; thus an *o*-carboxy-sulphinic acid may be condensed with a simple aromatic compound:

$$C_6H_4 <{}^{SO_2H}_{CO_2H} + C_6H_6 = C_6H_4 <{}^{S}_{CO}> C_6H_4 + 2H_2O + O.$$

but no experiments dealing with this method are described in the present paper, for a typical case has already been investigated (Davis and Smiles, Trans., 1910, **97**, 1290), when thioxanthone was prepared from *o*-carboxybenzenesulphinic acid and benzene.

The substances described in the experimental part of this paper are by no means the sole products of the various interactions; in fact, it is not easy with the usual methods to isolate the thioxanthones from the impure products, and were it not for the help of a method of fractional sublimation (Christopher, Proc., 1911, **27**, 236) it is doubtful whether these experiments could have been brought to a successful conclusion.

Experimental.

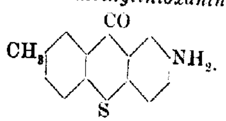
2-Aminothioxanthone, $C_6H_4 <{}^{CO}_{S}> C_6H_3 \cdot NH_2$.

An intimate mixture of 10 grams of *m*-aminobenzoic acid with 23 grams of benzenesulphinic acid was heated at 170—190° for four hours. The cold mass was boiled with aqueous sulphuric acid, and then, after being rendered alkaline with alkali hydroxide, the mixture was repeatedly extracted with ether. The united extracts were shaken with diluted sulphuric acid, and the aqueous layer,

which contained the sparingly soluble sulphate, was treated with alkali to liberate the base. The greenish-yellow precipitate was collected, and when dry it was sublimed in a vacuum. The product formed orange needles, which melted at 222°, whether heated alone or mixed with 2-aminothioxanthone obtained from another source (F. Mayer, *loc. cit.*). (Found, C = 68·8; H = 3·8. Calc., C = 68·7; H = 3·9 per cent.)

The substance also possessed the other physical properties elsewhere attributed to 2-aminothioxanthone.

2-Amino-7-methylthioxanthone,



The preparation of this substance from *m*-aminobenzoic acid and *p*-toluenesulphinic acid was conducted in the same manner as that described with 2-aminothioxanthone. However, the yields were extremely poor, and unfortunately an accident which occurred during the analysis of the small quantity available rendered invalid the estimation of hydrogen in this substance:

0·1366 gave 0·3506 CO_2. C = 70·0.

$C_{14}H_{11}ONS$ requires C = 69·71 per cent.

The substance forms orange needles, which melt at 190°, whilst other physical properties are similar to those of the 2-amino-derivative.

2-Hydroxy-7-methylthioxanthone,

$$C_6H_3Me{<}{\scriptstyle CO \atop S}{>}C_6H_3{\cdot}OH.$$

Interaction of 10 grams of *m*-hydroxybenzoic acid with 23 grams of *p*-toluenesulphinic acid was effected by heating the mixture at 130° during four hours. The cold mass was boiled with aqueous sodium hydroxide, and then the phenols were liberated from the solution by saturation with carbonic acid. The semi-solid precipitate was dissolved in ether, and the solution was shaken with excess of aqueous alkali hydroxide. A considerable quantity of material dissolved in the latter medium, forming a deep orange-coloured solution; this was kept for twenty-four hours, when the sparingly soluble sodium salt of the required thioxanthone separated in flocculent masses of needles. The hydroxythioxanthone obtained by treating this sodium salt with dilute mineral acid was almost pure, but it was further purified by sublimation in a vacuum. The

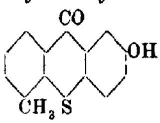
product, 2-hydroxy-7-methylthioxanthone, formed large, lemon-yellow* needles, which showed a metallic lustre; these melted at 217°, and dissolved in concentrated sulphuric acid, imparting a brilliant green fluorescence to that medium:

0·1149 gave 0·2910 CO_2 and 0·0426 H_2O. C=69·0; H=4·2.

$C_{14}H_{10}O_2S$ requires C=69·4; H=4·1 per cent.

The sodium salt of this substance separates in orange needles from an alkaline aqueous solution of the phenol. The latter is sparingly soluble in most cold organic media, but it may be recrystallised from hot acetic acid, in which it is moderately soluble.

2-Hydroxy-5-methylthioxanthone,



The preparation of this hydroxy-derivative was conducted in the manner described in the foregoing paragraph, *m*-hydroxybenzoic and *o*-toluenesulphinic acids being heated together in quantities of 10 and 23 grams respectively. The yields obtained were somewhat poorer than with *p*-toluenesulphinic acid, partly on account of the greater solubility of the sodium salt in the alkaline medium. The product was purified as usual by sublimation in a vacuum, when it was obtained in yellow needles, which melted at 211°:

0·0755 gave 0·1926 CO_2 and 0·029 H_2O. C=69·5; H=4·2.

$C_{14}H_{10}O_2S$ requires C=69·4; H=4·1 per cent.

Other physical properties of this substance are similar to those of the 7-methyl derivative.

Hydroxythioxanthone, $C_6H_4<^{CO}_{S}>C_6H_3\cdot OH$.

In some previous experiments (Davis and Smiles, *loc. cit.*) a hydroxythioxanthone was obtained by condensation of *o*-thiolbenzoic acid with phenol in the presence of warm concentrated sulphuric acid. Although by heating this substance water could not be expelled from it, the suggestion was offered that it crystallises with water, for repeated fractionation did not appreciably alter the composition. In view of the fact that the methyl derivatives do not crystallise in this manner, it was considered necessary to re-investigate the simpler substance in order to determine the cause of the apparent divergence of properties. It appeared probable that an oxide of the thioxanthone might have been present as an

impurity, for observations from numerous sources have shown that sulphides are apt to be oxidised on prolonged heating with sulphuric acid; but beyond fractional crystallisation, a method of removing substances of this type from the mixture could not be devised until the formation of the methyl derivatives from the sulphinic acids had been investigated. From the alkaline mother liquors whence the sodium salts of these substances had separated, more soluble salts were isolated by adding concentrated alkali hydroxide. The substances obtained from these by mineral acids resisted all attempts at complete purification; but there is little doubt that they are the oxides of the corresponding hydroxythioxanthones which have escaped reduction by the excess of the sulphinic acid. When heated in a vacuum at 200° they char and furnish a sublimate of the thioxanthone. The solubility of the sodium salts of these substances suggested a means of removing similar impurities from the crude hydroxythioxanthone, and the following method of preparation was adopted.

It was found that the yield of hydroxythioxanthone may be much improved by employing a relatively large quantity of phenol, for much of this substance is removed by sulphonation during the course of the interaction with *o*-thiolbenzoic acid. In other respects the condensation was effected as previously described. The product obtained by adding the mixture to water was dissolved in hot $2N$-alkali hydroxide, and on cooling the solution the sodium salt of hydroxythioxanthone separated in orange needles. These were collected, and washed with the cold medium, in which they are almost insoluble. The purified phenol was liberated from this sodium salt with mineral acid, and it was eventually sublimed in a vacuum at 200°:

0·1067 gave 0·2655 CO_2 and 0·3569 H_2O. C = 67·9; H = 3·7.

$C_{13}H_8O_2S$ requires C = 68·4; H = 3·5 per cent.

The *hydroxythioxanthone* thus obtained forms large, lemon-yellow needles, which exhibit a metallic lustre, and melt at 243°. The substance is very sparingly soluble in most cold organic media, and its orange-coloured sodium salt is almost insoluble in cold water.

In conclusion we desire to express our thanks to the Research Fund Committee of the Society for a grant which has defrayed the cost of these experiments.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

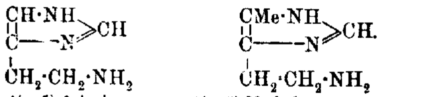
CCXXXII.—*Some Derivatives of* 4(*or* 5)-*Methylglyoxaline.*

By Arthur James Ewins.

The recent discovery of the high degree of physiological activity attaching to the base 4(or 5)-β-aminoethylglyoxaline (Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318) and its possible therapeutical importance, has served to stimulate research in the direction of glyoxaline derivatives generally. The most interesting result so far has been the synthesis and resolution of the biochemically important amino-acid histidine (α-amino-β-glyoxaline-4(or 5)-propionic acid) by Pyman (this vol., p. 1386), who has also devised a new synthetic method of preparing the base 4(or 5)-β-aminoethylglyoxaline (this vol., p. 668) in place of the tedious and expensive method employed by Windaus and Vogt (*Ber.*, 1907, **40**, 3691). Of the numerous derivatives obtained in the course of this work, however, none was found to be possessed of physiological activity in any marked degree.

Quite recently Windaus and Opitz (*Ber.*, 1911, **44**, 1721) have obtained the alcohol 4(or 5)-β-hydroxyethylglyoxaline corresponding with the active base already mentioned, and, moreover, have synthesised 4(or 5)-β-aminomethylglyoxaline, the lower homologue of this base. From experiments carried out in these laboratories, this new base has been found, however, to be almost devoid of physiological action.

The present communication deals in the main with the synthesis of a methyl homologue of 4(or 5)-β-aminoethylglyoxaline, namely, 4(or 5)-methyl-5(or 4)-β-aminoethylglyoxaline, which it was expected might prove physiologically interesting. The structural relationship of the two bases is best seen from the following formulæ:

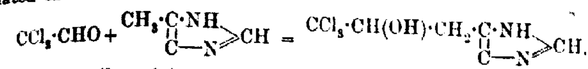


4(or 5)-β-Amino-ethylglyoxaline. 4(or 5)-Methyl-5(or 4)-β-amino-ethylglyoxaline.

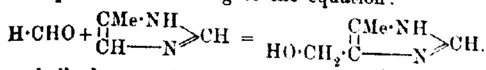
these bases in each case being tautomeric (compare Pyman, Trans., 1910, **97**, 1814).

The synthesis of this methyl homologue of 4(or 5)-β-aminoethylglyoxaline was suggested by an observation made by Windaus (*Ber.*, 1909, **42**, 758). It had been recorded by O. Gerngross (*Ber.*, 1909, **42**, 398) that 4(or 5)-methylglyoxaline on treatment with chloral formed an additive product, which he considered to be

4-γγγ-trichloro-β-hydroxypropylglyoxaline, the reaction being formulated thus:

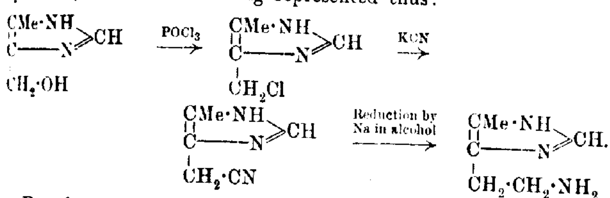


Windaus (*loc. cit.*), however, found that 4(or 5)-methylglyoxaline on treatment with formaldehyde yielded a product which on reduction gave 4:5-dimethylglyoxaline. The additive product must therefore be produced according to the equation:



The methylhydroxymethylglyoxaline so produced was not obtained by Windaus in a pure condition; but as the required 4(or 5)-methyl-5(or 4)-aminoethylglyoxaline should be readily obtainable from this hydroxy-derivative by a series of reactions analogous to those employed by Pyman in the conversion of 4(or 5)-hydroxymethylglyoxaline into 4(or 5)-β-aminoethylglyoxaline, the work of Windaus was repeated with a view to the isolation of 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline in the pure state. This was readily accomplished after slightly modifying the conditions of Windaus's experiment, and a good yield (50 per cent. of the theory) of the base was isolated by means of its pure, crystalline picrate.

The conversion of 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline into the required base was carried out on the lines of Pyman's synthesis, the reactions being represented thus:



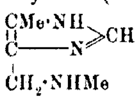
For the conversion of 4(or 5)-hydroxymethylglyoxaline into the corresponding chloro-derivative Pyman employed phosphorus pentachloride. This reagent was found to be unsuitable in the case of the methyl homologue. With the hydrochloride of the chloro-derivative no reaction occurred in the cold (compare Pyman), and with the free base, or on heating with the hydrochloride, a considerable amount of charring occurred. By employing phosphoryl chloride, however, the reaction proceeded quite smoothly, and a quantitative yield of the chloro-derivative was obtained.

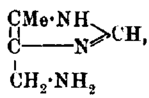
Like 4(or 5)-chloromethylglyoxaline, the methyl homologue is extremely reactive; thus on treating a freshly prepared ice-cold

aqueous solution of the base with a similarly cold solution of picric acid, a crystalline picrate was obtained, which was found to consist of nearly pure 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline picrate, the chlorine atom of the base having been replaced by hydroxyl by the action of the water even at 0°.

The conversion of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline into the corresponding cyano-compound and the reduction of the latter to the ethylamine base followed exactly on the lines of Pyman's synthesis.

By the action of cold aqueous methylamine and of cold concentrated aqueous ammonia on 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline, two other bases, namely, 4(or 5)-*methyl*-5(or 4)-*methylaminomethylglyoxaline* (I) and 4(or 5)-*methyl*-5(or 4)-*aminomethylglyoxaline* (II), were obtained, although the yields obtained were comparatively small (10—20 per cent.).


(I.)


(II.)

With the exception of 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline and of 4(or 5)-methyl-5(or 4)-β-aminoethylglyoxaline, all the glyoxaline derivatives obtained during the course of this investigation give an intense red colour with *p*-diazobenzenesulphonic acid in alkaline solution (Pauly's histidine reagent, *Zeitsch. physiol. Chem.*, 1904, **42**, 508). It may be also mentioned that it appears to be a general property of glyoxaline derivatives that they form phosphotungstates, which are soluble in hot water or cold acetone, and may usually be crystallised from dilute acetone, a property which is often of considerable advantage as a means of separation and purification.

The physiological action of the various bases obtained during the course of this work was investigated by Dr. P. P. Laidlaw, of these laboratories, to whom the author wishes to express his thanks. It was found that the bases 4(or 5)-methyl-5(or 4)-aminomethylglyoxaline and 4(or 5)-methyl-5(or 4)-methylaminomethylglyoxaline were physiologically almost inactive. 4(or 5)-Methyl-5(or 4)-β-aminoethylglyoxaline was, however, found to be physiologically active, chiefly in producing a decided fall in blood pressure (vasodilator effect) when injected intravenously, similar to, although somewhat less powerful than, that produced by 4(or 5)-β-aminoethylglyoxaline. It has also a motor effect on plain muscle, but its activity in this direction is far less (only about 1/200th or less) than that produced by the last-mentioned base.

EXPERIMENTAL.

Interaction of 4(or 5)-*Methylglyoxaline and Formaldehyde.*

Five grams of 4(or 5)-methylglyoxaline were heated in a sealed tube for two hours at 120° with 10 c.c. of a 40 per cent. solution of formaldehyde. There was no pressure on opening the tube, and to the clear, light yellow contents was added a hot saturated aqueous solution of 6·5 grams of picric acid. On cooling, a yellow, crystalline solid separated, which after recrystallisation from dilute (50 per cent.) alcohol was obtained quite pure. Yield, 9 grams.

4(or 5)-*Methyl*-5(or 4)-*hydroxymethylglyoxaline*,

$$\begin{matrix} CH_3\cdot C\cdot NH \\ \parallel \\ HO\cdot CH_2\cdot C—N \end{matrix} \!\!> CH.$$

The free base was obtained from the picrate by converting the latter into the hydrochloride, and treating the solution so obtained with excess of sodium carbonate. The alkaline solution was evaporated to dryness, the residue extracted with absolute alcohol, and the solution concentrated. On keeping, the crystalline base slowly separated in stout, hexagonal prisms, melting at 138°:

0·1568 gave 0·3074 CO_2 and 0·1002 H_2O. C=53·5; H=7·1.
0·3084 „ 68·2 c.c. N_2 (moist) at 23° and 758 mm. N=25·2.
$C_5H_8ON_2$ requires C=53·6; H=7·1; N=25·0 per cent.

The base is very readily soluble in water or alcohol, but sparingly so in most other organic solvents. Solutions of the base or of its salts give an intense cherry-red coloration with *p*-diazobenzenesulphonic acid. In neutral or alkaline solution it gives a precipitate with mercuric chloride, which is soluble in dilute acid. With phosphotungstic acid solution it gives a precipitate, which is readily soluble in hot water or cold acetone, and may readily be crystallised from dilute acetone, forming fan-shaped clusters of short, broad prisms.

The *hydrochloride*, obtained from the picrate in the usual manner, crystallises from absolute alcohol, the yield being increased by addition of a little dry ether. It forms stout, hexagonal plates, melting at 240—242°. The salt is deliquescent, and readily soluble in water or alcohol:

0·1658 gave 0·2440 CO_2 and 0·0892 H_2O. C=40·1; H=5·9.
0·1340 „ 22·4 c.c. N_2 (moist) at 23° and 758 mm. N=19·0.
0·1580 „ 0·1524 AgCl. Cl=23·8.
$C_5H_8ON_2$,HCl requires C=40·3; H=6·0; N=18·8; Cl=24·0 per cent.

The *picrate* obtained as described above crystallises from hot 50 per cent. alcohol in long, thin prisms, melting to a red liquid at 180—181°:

0·1374 gave 0·1938 CO_2 and 0·0410 H_2O. C=38·5; H=3·3.

0·2596 „ 47·2 c.c. N_2 (moist) at 25° and 766 mm. N=20·8.

$C_5H_8ON_2,C_6H_3O_7N_3$ requires C=38·7; H=3·2; N=20·6 per cent.

This salt is very sparingly soluble in cold water or alcohol, but fairly readily so in these solvents when hot.

4(or 5)-*Methyl*-5(or 4)-*chloromethylglyoxaline*,

$$\begin{array}{l} CH_3\cdot C\cdot NH \\ \quad\quad\;\; \| \\ CH_2Cl\cdot C—N \end{array}\!\!>\!CH.$$

The *hydrochloride* of this base was readily obtained as follows: Five grams of 4(or 5)-methyl-5(or 4)-hydroxymethylglyoxaline hydrochloride were suspended in about 20 c.c. of phosphoryl chloride, and the mixture gently warmed on a sand-bath under a reflux condenser. Hydrogen chloride was evolved, and solution was complete in about fifteen minutes. The excess of phosphoryl chloride was removed by distillation in a vacuum, and the residual syrupy liquid dissolved in a small quantity of hot saturated alcoholic solution of hydrogen chloride. On cooling, the crystalline hydrochloride of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline rapidly separated. Precipitation was completed by the addition of a little dry ether. For analysis the salt was recrystallised from absolute alcohol. It forms thin, rectangular plates, melting at 222°. The yield is quantitative:

0·0776 gave 0·1014 CO_2 and 0·0328 H_2O. C=35·6; H=4·7.

0·0996 „ 0·1718 AgCl. Cl=42·7.

$C_5H_7N_2Cl,HCl$ requires C=35·9; H=4·8; Cl=42·5 per cent.

This salt is very readily soluble in cold methyl alcohol.

4(or 5)-*Methyl*-5(or 4)-*cyanomethylglyoxaline*,

$$\begin{array}{l} \quad\quad\;\; CH_3\cdot C\cdot NH \\ \quad\quad\quad\quad\quad\;\; \| \\ CN\cdot CH_2\cdot C—N \end{array}\!\!>\!CH.$$

This substance was prepared from the corresponding chloro-derivative by the method which was found by Pyman (*loc. cit.*) to yield the best results with 4(or 5)-chloromethylglyoxaline. Fifteen grams of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline hydrochloride were dissolved in 180 c.c. of absolute alcohol, and the solution slowly directed drop by drop to a solution of 50 grams of potassium cyanide in about 60 c.c. of water. The mixture was kept well stirred and [illegible] temperature of 0°. The precipitated salts were collected, [illegible] with alcohol, and the filtrate and washings treated with

30 c.c. of saturated sodium carbonate solution. The mixture was evaporated to dryness under diminished pressure, the residue extracted with warm ethyl acetate, and the solvent evaporated. From the residual brown, syrupy liquid the 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline crystallised out on keeping. Yield, 2·7 grams (24 per cent. of the theoretical).

For analysis the base was recrystallised from water, when it was obtained in large, rectangular prisms, melting at 163—164°:

0·2274 gave 0·4954 CO_2 and 0·1264 H_2O. C = 59·4; H = 5·7.

0·1194 „ 34·0 c.c. N_2 (moist) at 15° and 772 mm. N = 34·7.

$C_6H_7N_3$ requires C = 59·5; H = 5·8; N = 34·7 per cent.

4(or 5)-*Methyl*-5(or 4)-*cyanomethylglyoxaline* is moderately soluble in cold, and very readily so in hot, water. Solutions of the base give with mercuric chloride a white precipitate, soluble in dilute acids. The *phosphotungstate* of the base is almost insoluble in cold water, but readily soluble in hot water or cold acetone. It crystallises from dilute acetone in long needles. With *p*-diazobenzenesulphonic acid in alkaline solution (sodium carbonate) an intense deep reddish-brown coloration is produced, the colour being strikingly different from that usually given by simple glyoxaline derivatives.

The *picrate* crystallises from hot water in prisms melting at 172°.

4(or 5)-*Methyl*-5(or 4)-β-*aminoethylglyoxaline*,

$$\begin{array}{l} \qquad\qquad\quad CH_3\cdot C\cdot NH \\ \qquad\qquad\qquad\quad \| \qquad\quad >CH. \\ NH_2\cdot CH_2\cdot CH_2\cdot C—N \end{array}$$

The reduction of 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline to the required base was carried out by means of sodium in concentrated alcoholic solution.

2·5 Grams of 4(or 5)-methyl-5(or 4)-cyanomethylglyoxaline were dissolved in a minimum quantity of absolute alcohol, and 6·5 grams of sodium was added in small portions to the gently boiling solution. Alcohol was added from time to time as necessary. The solution was then made acid to Congo-red by addition of concentrated hydrochloric acid, and the precipitated salt collected. The filtrate was rendered alkaline with sodium carbonate, evaporated to dryness, and dissolved in a little absolute alcohol. On keeping, nothing separated out, and the solution was then treated with a hot saturated solution of picric acid. The crystalline *picrate* of 4(or 5)-methyl-5(or 4) - β - aminoethylglyoxaline rapidly separated. Yield, 2·7 grams (22 per cent. of the theoretical):

0·1594 gave 0·2158 CO_2 and 0·0402 H_2O. C = 36·9; H = 2·8.

0·1100 „ 20·2 c.c. N_2 (moist) at 19° and 761 mm. N = 21·2.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C = 37·0; H = 2·9; N = 21·6 per cent.

The *dihydrochloride* crystallises from absolute alcohol in colourless, prismatic needles, melting at 231—232°:

0·1295 gave 0·1732 CO_2 and 0·0801 H_2O. C=36·5; H=6·8.

$C_6H_{11}N_3,2HCl$ requires C=36·7; H=6·6 per cent.

This salt is anhydrous, very sparingly soluble in hot absolute alcohol, very readily so in cold water, and fairly readily so in cold methyl alcohol. With *p*-diazobenzenesulphonic acid in alkaline solution a reddish-yellow colour is produced. The aqueous solution of the salt is precipitated by mercuric chloride, the precipitate being soluble in dilute acids. The phosphotungstate of the base is readily soluble in hot water or in cold acetone.

The *dihydrobromide* crystallises from absolute alcohol, on addition of dry ether, in stout, hexagonal prisms, melting at 212°:

0·1028 gave 0·1348 AgBr. Br=55·8.

$C_6H_{11}N_3,2HBr$ requires Br=55·8 per cent.

4(or 5)-*Methyl*-5(or 4)-*methylaminomethylglyoxaline*,

$$\begin{array}{l} \qquad\qquad\quad CH_3{\cdot}C{\cdot}NH \\ \qquad\qquad\qquad\ \| \qquad\quad >CH. \\ CH_3{\cdot}NH{\cdot}CH_2{\cdot}C{-\!\!-}N \end{array}$$

This base was obtained by the action of methylamine on 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline.

0·5 Gram of 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline was dissolved in a few c.c. of methyl alcohol, and the solution added drop by drop to 2·5 c.c. of an aqueous solution of methylamine, which was kept at a temperature of about 0°. The solution was then evaporated to dryness, the residue dissolved in a little water, and treated with a hot saturated aqueous solution of picric acid. The heavy, yellow oil which separated from the hot solution was collected, and from the filtrate on cooling the crystalline 4(or 5)-*methyl*-5(or 4)-*methylaminomethylglyoxaline dipicrate* separated. It crystallises from water in prisms melting at 222°. Yield, 20 per cent. of theory:

0·1218 gave 0·1654 CO_2 and 0·0352 H_2O. C=37·0; H=3·2.

0·0944 „ 17·4 c.c. N_2 (moist) at 16° and 764 mm. N=21·6.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C=37·0; H=2·9; N=21·6 per cent.

The *dihydrochloride* crystallises from absolute alcohol in stout prisms, melting at 246—247°:

0·1014 gave 0·1480 AgCl. Cl=36·1.

$C_6H_{11}N_3,2HCl$ requires Cl=36·2 per cent.

4(or 5)-*Methyl*-5(or 4)-*aminomethylglyoxaline*,

$$\begin{array}{l} CH_3\cdot C\cdot NH \\ \quad\;\; \| \\ NH_2\cdot CH_2\cdot C—N \end{array}\!\!>\!CH.$$

This base was obtained from 4(or 5)-methyl-5(or 4)-chloromethylglyoxaline by the method employed for the preparation of the foregoing base, using concentrated aqueous ammonia (0·88) in place of methylamine. The yield of base was very poor, amounting to only 10 per cent. of the theory.

The *picrate* crystallises from hot water in clusters of well-formed prisms, melting at 216—217°:

0·0934 gave 0·1224 CO_2 and 0·0240 H_2O. C = 35·7; H = 2·8.

$C_5H_9N_3,(C_6H_3O_7N_3)_2$ requires C = 35·8; H = 2·6.

The *hydrochloride* crystallises from absolute alcohol in stout, rectangular prisms, melting at 233—234°.

Solutions both of this and of the foregoing base give with *p*-diazobenzenesulphonic acid an intense cherry-red colour.

The greater part of the analytical work in connexion with this investigation has been carried out by Mr. C. J. Gobell, to whom the author wishes to express his thanks.

THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
HERNE HILL, LONDON, S.E.

CCXXXIII.—*The Triazo-group. Part XIX. Nitroso-azides of Dipentene,* d-*Limonene, and* l-*Limonene.*

By MARTIN ONSLOW FORSTER and FREDERIK MARINUS VAN GELDEREN.

IT has been shown that the nitrosate of trimethylethylene readily exchanges the $O\cdot NO_2$-group for the azoimide nucleus (this vol., p. 239), yielding the oxime of the triazoketone,

$$(CH_3)_2CN_3\cdot CO\cdot CH_3,$$

and that the nitrosochlorides of pinene and terpineol undergo a similar transformation into the corresponding nitrosoazides (*loc. cit.*, p. 244). α-Triazocamphoroxime (Trans., 1907, **91**, 874), although obtained by a different process, may be looked upon as the earliest representative of this class, and with the object of gaining further information as to the applicability of the reaction above indicated,

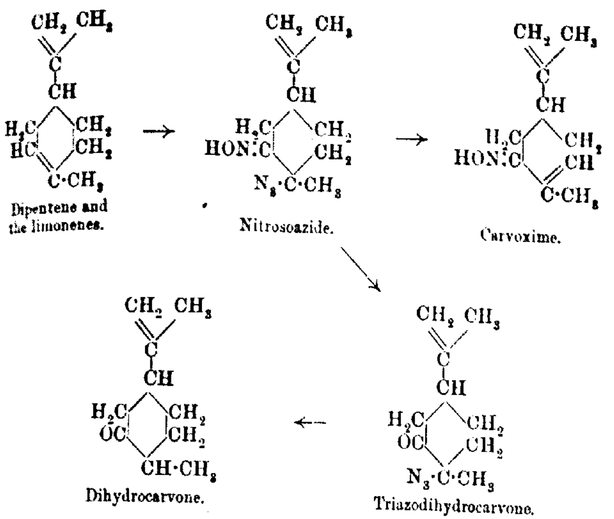
and the behaviour of the triazo-group in the products, we have prepared nitrosoazides of dipentene, *d*-limonene, and *l*-limonene.

The first point brought to light is the facility with which dipentene nitrosate yields the nitrosoazide, the proportion of which is greatly in excess of that derived from trimethylethylene nitrosate, and in this respect it resembles pinene nitrosochloride. Dipentene nitrosochloride also lends itself with great readiness to interaction, but the limonene nitrosoazides are associated with such a large proportion of oily by-products that the yield sinks to the neighbourhood of 20 per cent. A similar difficulty was encountered by Leach (Trans., 1905, **87**, 413) in connexion with the limonene nitrosocyanides, which were accompanied by 60 per cent. of oil, even in the most favourable circumstances.

The well-known experiments of Wallach (*Annalen*, 1889, 252, 113, and 1892, **270**, 181) dealing with the preparation of nitrolamines from the limonene nitrosochlorides, coupled with the fact that Leach isolated the α- and β-nitrosocyanides, led to the expectation that the isomeric nitrosoazides would be obtainable from each hydrocarbon; in this we were disappointed, however, only one derivative being isolated alike from the α- and the β-nitrosochlorides. As Leach's experiments showed that the yield of β-nitrosocyanide amounted to only 2 or 3 per cent., it is probable that the missing nitrosoazide is concealed in the large proportion of oil with which the crystalline product is associated.

The correspondence in structure between the new nitrosoazides and the nitrosocyanides follows from their chemical behaviour. The presence of the *iso*nitroso-group is demonstrated by interaction with phenylcarbimide, although benzoyl and acetyl derivatives could not be isolated in solid form. Removal of the elements of hydrazoic acid leads to the respective carvoxime, whilst application of Wallach's process of hydrolysis (*Annalen*, 1906, **346**, 231) eliminates the oximino-group, and gives rise to the corresponding triazodihydrocarvone.

As appears from the formula on p. 2061, triazodihydrocarvone belongs to the class of triazoketones in which the triazotised carbon atom is tertiary, and in accordance with the principles already developed, distinguishes itself from triazocamphor and triazoacetone in its behaviour towards alcoholic alkali hydroxide, which does not set free two-thirds the azidic nitrogen, but eliminates the triazo-group in the form of alkali azide. It has been prepared in three forms, inactive from dipentene, and having strong dextro- and lævorotatory power when produced from *d*- and *l*-limonenes respectively. Their oximes are, of course, the nitrosoazides from which the ketones are directly obtainable by hydrolysis; the triazoketones



yield also well-crystallised semicarbazones, but we have not been able to prepare thiosemicarbazones, semioxamazones, or phenylhydrazones. The following table summarises the physical properties of the compounds under discussion:

	Inactive.	Dextrorotatory.	Lævorotatory.
Triazodihydrocarvone	b. p. 81°/0·4 mm.	b. p. 93°/0·46 mm.	b. p. 93—94°/0·48 mm.
Oxime	m. p. 72—73°	m. p. 52—53°	m. p. 52—53°
Phenylcarbamyloxime	m. p. 113—114°	m. p. 114—115°	m. p. 114—115°
Semicarbazone	m. p. 132—133°	m. p. 220°	m. p. 220°

It was to be expected that the reduction of triazodihydrocarvone would lead to the unknown aminoketone, or at least to the dihydropyrazine derivative corresponding with it, this alternative having been rendered probable by our experiments with the ketone from trimethylethylene nitrosoazide (this vol., p. 243). The action, however, takes a different course. Elemental nitrogen is eliminated, but the resulting aminoketone immediately loses its amino-group, which is exchanged for hydrogen, dihydrocarvone being the product. This unexpected result recalls the experience of Wallach (*Annalen*, 1898, **300**, 290, and 1900, **313**, 368), who encountered the same ketone among the products of reduction of the dibromide of nitrosopinene.

Experimental.

Dipentene Nitrosoazide, $C_{10}H_{15}(:NOH)\cdot N_3$.

The hydrocarbon used for these experiments boiled at 174—176°, had D^{15} 0·8653, and gave α_D 2°42′ in a 2-dcm. tube, whence $[\alpha]_D$ 1·5[illegible]. It was converted into the nitrosate and the nitrosochloride by the recognised methods, either of these materials being suitable for transformation into the nitrosoazide.

Twenty-five grams of the additive compound were covered with 50 c.c. of alcohol and a concentrated aqueous solution of sodium azide containing 15 grams; during seven days the suspended matter gradually passed into solution, crystals of sodium chloride or nitrate appearing. On pouring the mixture into cold water, the turbid product deposited crystals, the yield of nitrosoazide representing more than 80 per cent. of the theoretical amount; as the nitrosochloride of dipentene is a more economical product than the nitrosate, and there does not appear to be any difference between the two substances in their behaviour towards sodium azide, the nitrosochloride was always employed in the later experiments:

0·2513 gave 57·1 c.c. N_2 at 17° and 777 mm. N = 27·34.

$C_{10}H_{16}ON_4$ requires N = 26·92 per cent.

The substance is readily soluble in organic solvents, and is best crystallised from methyl alcohol, which deposits lustrous, rhombic plates, melting at 72—73°. It effervesces vigorously with concentrated sulphuric acid, and somewhat slowly with stannous chloride in hydrochloric acid, liberation of gas becoming more marked on warming. The nitrosoazide is volatile in steam, and is not dissolved by aqueous alkalis, which fail to remove either the oximino- or the triazo-group; with alcoholic alkali hydroxide, however, the elements of hydrazoic acid are eliminated, the product being inactive carvoxime, m. p. 93°.

The *phenylcarbamyl* derivative, $C_{10}H_{15}(:NO\cdot CO\cdot NH\cdot C_6H_5)\cdot N_3$, prepared by mixing molecular proportions of dipentene nitrosoazide and phenylcarbimide in dry benzene, crystallised in needles on adding petroleum, and after recrystallisation from boiling petroleum melted at 113—114°:

0·1006 gave 18·7 c.c. N_2 at 23° and 769 mm. N = 21·69.

$C_{17}H_{21}O_2N_5$ requires N = 21·40 per cent.

The substance is insoluble in cold petroleum, but dissolves readily in the hot liquid and in cold alcohol, ether, or benzene.

i-Triazodihydrocarvone, $\genfrac{}{}{0pt}{}{CH_2}{CH_3}\!>\!C\cdot CH\!<\!\genfrac{}{}{0pt}{}{CH_2-CO}{CH_2\cdot CH_2}\!>\!C\!<\!\genfrac{}{}{0pt}{}{CH_3}{N_3}$.

Attempts to hydrolyse dipentene nitrosoazide with mineral acids having shown that carvacrol is produced, the triazoketone was prepared by the action of hot aqueous oxalic acid. In quantities of 5 grams the oxime was mixed with oxalic acid (15 grams) in concentrated solution, when a current of steam carried over about 50 per cent. of a colourless oil, which was extracted with ether, dried with sodium sulphate, and distilled with the Gaede pump:

0·1740 gave 32·8 c.c. N_2 at 18° and 756 mm. N = 22·00.

$C_{10}H_{15}ON_3$ requires N = 21·76 per cent.

The triazoketone has a pleasant odour of peppermint, and rapidly becomes yellow, even when protected from light; it boils at 81° 0·4 mm., and has D^{20} 1·0409. Although effervescence with concentrated sulphuric acid is very vigorous, action with stannous chloride is sluggish, even on warming, and alkalis do not liberate nitrogen. When heated in alcohol with hydroxylamine acetate the triazoketone regenerates the nitrosoazide.

The *semicarbazone*, $C_{10}H_{15}(:N\cdot NH\cdot CO\cdot NH_2)\cdot N_3$, prepared from *i*-triazodihydrocarvone and semicarbazide acetate in dilute alcohol, separates rapidly, and after crystallisation from benzene diluted with petroleum melts at 132—133°:

0·1450 gave 42·9 c.c. N_2 at 16° and 747 mm. N = 34·30.

$C_{11}H_{18}ON_6$ requires N = 33·60 per cent.

The substance is freely soluble in ordinary solvents, excepting petroleum.

Reduction with Aluminium Amalgam.—In the hope of obtaining the aminoketone, *i*-triazodihydrocarvone was reduced in moist ether with aluminium amalgam. Nitrogen was liberated, and about 70 per cent. of non-basic material was produced; this yielded an oxime, which after recrystallisation from alcohol melted at 112—113°:

0·1147 gave 0·3020 CO_2 and 0·1069 H_2O. C = 71·81; H = 10·43.
0·1649 „ 12·15 c.c. N_2 at 16° and 766 mm. N = 8·77.

$C_{10}H_{17}ON$ requires C = 71·86; H = 10·18; N = 8·38 per cent.

On searching for substances having this composition, it was found that the properties of the oxime correspond with those of dihydrocarvoxime (Wallach, *Annalen*, 1898, **300**, 290, and 1900, **313**, 368). Hence the principal effect of reduction is to replace the triazo-group by hydrogen, a result which is quite unusual, and the aminoketone could not be recognised. A very small quantity of a basic substance was produced, however, melting at 125°, and forming a platini-

chloride decomposing at 217°; owing to insufficiency of material it could not be investigated further, but is probably the dihydro-pyrazine derivative corresponding with that obtained from amino-camphor and from β-triazo-β-methylbutan-γ-one (this vol., p. 239).

d-*Limonene Nitrosoazide*, $C_{10}H_{15}(:NOH)\cdot N_3$.

The specimen of *d*-limonene employed had D^{18} 0·8474, and gave α_D 102°15′ in a 1-dcm. tube, whence $[\alpha]_D$ 120·6°. It was converted into the nitrosochlorides, which were then separated in order to ascertain whether the β-nitrosochloride gave a triazo-compound distinct from that into which the α-nitrosochloride is converted. No difference being recognised, the mixture of nitrosochlorides was used in subsequent experiments; the conditions of transformation into the nitrosoazide were the same as those observed in the preparation of dipentene nitrosoazide, excepting that the product was extracted with ether instead of being allowed to crystallise from the diluted alcoholic solution. The yield, however, was greatly inferior to that obtained from the inactive hydrocarbon, for the crystals deposited on evaporating the ether amounted to between 20 and 40 per cent. of the theoretical quantity, the remainder persisting as an oil. After recrystallisation from diluted methyl alcohol, the substance melted at 52—53°:

0·2283 gave 51·3 c.c. N_2 at 16° and 780 mm. N = 27·27.

$C_{10}H_{16}ON_4$ requires N = 26·92 per cent.

A solution containing 0·2970 gram, made up to 25 c.c. with chloroform, gave α_D 0°14′ in a 3-dcm. tube, whence $[\alpha]_D$ 6·5°. It dissolves readily in the ordinary organic solvents, but is difficult to crystallise. The behaviour towards sulphuric acid and towards stannous chloride is the same as that of the inactive azide, and alcoholic alkali hydroxide gives rise to *l*-carvoxime, melting at 71—72°, and having $[\alpha]_D$ −33°.

The *phenylcarbamyl* derivative, $C_{10}H_{15}(:NO\cdot CO\cdot NH\cdot C_6H_5)\cdot N_3$.—Although attempts to benzoylate or acetylate the nitrosoazide did not lead to a solid product, phenylcarbimide was found to act readily on the substance in dry benzene, which was subsequently evaporated under reduced pressure until crystallisation began, when the residue was dissolved in methyl alcohol; this yielded crystals on slow evaporation following slight dilution, but the substance was much more difficult to isolate than the inactive isomeride. Recrystallisation from hot petroleum gave lustrous, transparent prisms, melting at 114—115°:

0·1508 gave 28·3 c.c. N_2 at 23° and 763 mm. N = 21·73.

$C_{17}H_{21}O_2N_5$ requires N = 21·40 per cent.

A solution containing 0·2769 gram, made up to 25 c.c. with chloroform, gave α_D 3°57′ in a 3-dcm. tube, whence $[\alpha]_D$ 118·8°. The substance is freely soluble in cold solvents, excepting petroleum, from which, on slow evaporation, it crystallises in inch-long prisms; it effervesces vigorously with concentrated sulphuric acid, and more moderately with stannous chloride in hydrochloric acid.

d-*Triazodihydrocarvone*, $C_{10}H_{15}ON_3$.

The ketone was prepared by hydrolysing *d*-limonene nitrosoazide with hot aqueous oxalic acid, being carried over in steam, and isolated in the usual manner:

0·1908 gave 35·4 c.c. N_2 at 16° and 762 mm. N = 21·98.

$C_{10}H_{15}ON_3$ requires N = 21·76 per cent.

The substance boils at 93°/0·46 mm., has D^{20} 1·0487, and gave α_D 92°48′ in a 1-dcm. tube, whence $[\alpha]_D$ 88·49°; a solution containing 0·8234 gram, diluted to 20 c.c. with chloroform, gave α_D 11°40′ in a 3-dcm. tube, whence $[\alpha]_D$ 94·4°. In chemical behaviour the ketone resembles the inactive one obtained from dipentene, and when it is heated with hydroxylamine acetate in aqueous alcohol the oxime (*d*-limonene nitrosoazide) is regenerated, m. p. 52—53°.

The *semicarbazone*, $C_{10}H_{15}(:N\cdot NH\cdot CO\cdot NH_2)\cdot N_3$, prepared in the usual manner, showed a tendency to remain viscid; on warming with water, however, the oily impurities were removed, the white solid being then dissolved in glacial acetic acid, and precipitated with water. This treatment was repeated until the melting point was constant at 220°, decomposition occurring at this temperature:

0·2864 gave 83·0 c.c. N_2 at 19° and 761 mm. N = 33·92.

$C_{11}H_{18}ON_6$ requires N = 33·60 per cent.

The substance is freely soluble in ordinary solvents, excepting cold petroleum.

Reduction with Aluminium Amalgam.—As in the case of the inactive triazoketone, the principal product of reduction with aluminium amalgam in moist ether was a ketone free from nitrogen; on converting this into its oxime, the latter was found to melt at 88—89°, and appears to be identical with the active dihydrocarvoxime described by Wallach (*Annalen*, 1893, **275**, 117). Associated with the liquid product was a very small proportion of a crystalline substance melting at 110—112°, and yielding a crystalline platinichloride.

l-*Limonene Nitrosoazide*, $C_{10}H_{15}(:NOH)\cdot N_3$.

The hydrocarbon used for the preparation of the nitrosochloride had D^{18} 0·8465, and gave α_D $-96°21'$ in a 1-dcm. tube, whence $[\alpha]_D$ $-113·8°$. Proceeding as in the case of the dextrorotatory compound, the yield was again found to be very poor, a large proportion of oily by-products accompanying the solid nitrosoazide, which was recrystallised from diluted methyl alcohol, and melted at 52—53°:

0·0964 gave 23·5 c.c. N_2 at 23° and 758 mm. N = 27·56.

$C_{10}H_{16}ON_4$ requires N = 26·92 per cent.

We have not been able to produce a specimen of this substance with optical activity corresponding with that of the dextrorotatory isomeride; a solution containing 0·3038 gram, made up to 25 c.c. with chloroform, gave only $-2'$ in the 3-dcm. tube, whence $[\alpha]_D$ less than $-1°$.

The *phenylcarbamyl* derivative, $C_{10}H_{15}(:NO\cdot CO\cdot NH\cdot C_6H_5)\cdot N_3$, prepared from *l*-limonene nitrosoazide and phenylcarbimide in benzene, remained as a syrup on evaporating the solvent under reduced pressure, but treatment as before with diluted methyl alcohol followed by hot petroleum gave lustrous, woolly needles melting at 114—115°:

0·0813 gave 15·3 c.c. N_2 at 23° and 765 mm. N = 21·84.

$C_{17}H_{21}O_2N_5$ requires N = 21·40 per cent.

A solution containing 0·2967 gram, made up to 25 c.c. with chloroform, gave α_D $-4°18'$ in a 3-dcm. tube, whence $[\alpha]_D$ $-120°$. The behaviour towards solvents, stannous chloride, and concentrated sulphuric acid is the same as that of the dextrorotatory modification.

l-*Triazodihydrocarvone*, $C_{10}H_{15}ON_3$.

Preparation of this triazoketone was effected by the oxalic acid method, about 60 per cent. of the amount expected being obtained:

0·1523 gave 28·6 c.c. N_2 at 18° and 761 mm. N = 22·05.

$C_{10}H_{15}ON_3$ requires N = 21·76 per cent.

The substance boils at 93—94°/0·48 mm., has D^{20} 1·0472, and gave α_D $-96°50'$ in a 1-dcm. tube at the same temperature, whence $[\alpha]_D$ $-92·47°$; a solution containing 0·8278 gram, diluted to 20 c.c. with chloroform, gave α_D $-11°42'$ in a 3-dcm. tube, whence $[\alpha]_D$ $-94·22°$. No chemical differences between this and the foregoing triazoketones were noticed, and hydroxylamine acetate regenerated *l*-limonene nitrosoazide, m. p. 52—53°.

The *semicarbazone*, $C_{10}H_{15}(:N\cdot NH\cdot CO\cdot NH_2)\cdot N_3$, resembled that

f the dextrorotatory triazoketone in its tendency to remain viscid, ut was purified by similar treatment, and melted and decomposed t 220°:

0·1432 gave 41·0 c.c. N_2 at 18° and 762 mm. N = 33·67.

$C_{11}H_{18}ON_6$ requires N = 33·60 per cent.

The substance is freely soluble in the ordinary solvents, excepting old petroleum.

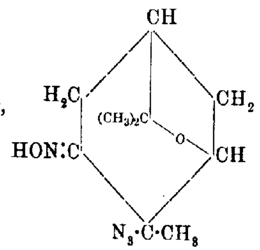
Reduction with Aluminium Amalgam.—Treating *l*-triazodihydro-arvone with aluminium amalgam in moist ether led to a result imilar to that recorded for the dextrorotatory and inactive triazo-ompounds. The principal product was a non-nitrogenous ketone, dentified by means of its oxime with *l*-dihydrocarvone (Wallach nd Schrader, *Annalen*, 1894, **279**, 381), along with a minute uantity of a basic solid.

onversion of the Active Compounds into Derivatives of Dipentene.

Equal amounts of *d*- and *l*-limonene nitrosoazides (m. p. 52—53°) ere mixed in methyl alcohol, heated on the water-bath during a hort period, and allowed to cool, when the characteristic crystals f dipentene nitrosoazide separated in the course of a few hours; he substance melted at 72—73°, and did not depress the melting oint of the nitrosoazide prepared from dipentene.

The *d*- and *l*-triazodihydrocarvones were mixed in ethyl alcohol, nd transformed into the semicarbazone, which melted at 132—133° fter crystallisation from a mixture of benzene and petroleum; it as identical with the semicarbazone prepared from *i*-triazodihydro-arvone.

Pinol Nitrosoazide,



Pinol, prepared by the action of sodium ethoxide on terpineol ibromide, was converted into the nitrosochloride, this being sus-ended in dilute alcohol containing sodium azide in the proportion f 4 to 9, and allowed to remain at 40° during half an hour, when e liquid had become clear; very soon afterwards lustrous crystals parated, and after recrystallisation from hot alcohol melted t 160°:

0·1866 gave 0·3704 CO_2 and 0·1231 H_2O. C=54·13; H=7·38.
0·1314 „ 28·3 c.c. N_2 at 20° and 767 mm. N=25·34.
$C_{10}H_{16}O_2N_4$ requires C=53·57; H=7·14; N=25·00 per cent.

The substance is remarkably stable for a member of this class, undergoing no change when heated with aqueous oxalic acid, from which it slowly passes over in the steam; moreover, when heated under reflux during three to four hours with dilute sulphuric acid and a few c.c. of alcohol, the greater part was recovered unchanged, and the liquid exerted only feeble reducing action on Fehling's solution. It dissolves in concentrated hydrochloric acid when gently heated, being precipitated on dilution, and, in consequence, we failed to isolate the corresponding triazoketone.

In conclusion, we wish to express our indebtedness to Sir William Tilden and to Messrs. Schimmel and Co. for valuable specimens with which they were so kind as to furnish us.

Royal College of Science, London.
South Kensington, S.W.

CCXXXIV.—*Preparation of the Betaine of Tryptophan and its Identity with the Alkaloid Hypaphorine.*

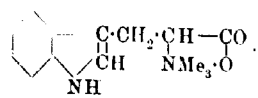
By Pieter van Romburgh and George Barger.

While working in the Botanic Gardens at Buitenzorg, in Java, the late Dr. M. Greshoff (*Mededeelingen uit 's Lands Plantentuin*, 1890, 7, 29) discovered a crystalline base in the seeds of *Erythrina Hypaphorus*, Boerl., a tree grown for the sake of its shade in the coffee plantations of Eastern Java. The base occurs in the seeds to the extent of about 3 per cent., and to this "alkaloid," for which the name "hypaphorine" was suggested, the formula $C_{14}H_{16}O_2N_2$ was assigned in the "Index Phytochemicus," a list of plant substances published in 1905 by Ritsema and Sack, under the auspices of the Colonial Museum at Haarlem.

In 1891, while still at Buitenzorg, one of us (P. v. R.), at Dr. Greshoff's request, had already joined him in the investigation of the constitution of the new base, and deduced the formula $C_{14}H_{18}O_2N_2$ for it, and had further, after Dr. Greshoff's return to Holland in 1892, shown that on heating with aqueous potassium hydroxide it yielded trimethylamine and indole. The work, subsequently interrupted for many years, was resumed after Dr. Greshoff's death. The results already referred to suggested that

hypaphorine might be a betaine derived from tryptophan, and on methylating a small quantity of this amino-acid, a base was indeed obtained which showed great similarity to hypaphorine (van Romburgh, *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **13**, 1177). Starting from the same view as to the probable constitution of hypaphorine, the other of us working with larger quantities of tryptophan, independently prepared the same trimethyl derivative.

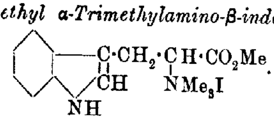
We have now obtained complete proof of the identity of hypaphorine with the betaine formed by methylating tryptophan, so that the alkaloid is α-trimethyl-β-indolepropiobetaine of the following constitution:



Hypaphorine is therefore a base of considerable biochemical interest. It is the first naturally occurring simple derivative of tryptophan. The absence of any pronounced physiological action and its great solubility in water differentiate it from the typical alkaloids (some of which, like strychnine and brucine, are possibly derived from tryptophan by complicated reactions). On the other hand, hypaphorine is a new member of the group of naturally occurring betaines, to which more attention has lately been directed, chiefly owing to the work of E. Schulze and his pupils. In addition to betaine itself, and to hypaphorine, this group at present contains stachydrine, trigonelline, and possibly also trimethylhistidine. The circumstance that hypaphorine is present in the seed to the extent of 3 per cent., and is readily isolated as the nitrate, might perhaps be utilised in a study of the metabolic importance of betaines in the plant, particularly in order to test the view expressed by Winterstein and Trier ("Die Alkaloide," 1910, p. 296) that betaines are merely waste products rendered innocuous by methylation. This question is the more interesting since Staněk (*Zeitsch. physiol. Chem.*, 1911, **72**, 402) has recently arrived at the conclusion that betaine itself is utilised as plastic material in the young shoots and leaves of various plants.

Experimental.

Iodide of Methyl α-Trimethylamino-β-indolepropionate,



This ester is the first reaction product which could be isolated when tryptophan was treated with methyl iodide and sodium

hydroxide according to Engeland's method (*Ber.*, 1910, **43**, 2662). One gram of tryptophan was dissolved in 25 c.c. of methyl alcohol and enough sodium hydroxide to render the solution slightly alkaline. After the addition of 25 c.c. of methyl iodide, the solution was gently boiled for eight hours under a reflux condenser; occasionally a little sodium hydroxide in methyl alcohol was added, in order to keep the reaction alkaline. Finally, the solution was evaporated; the residual syrup at once crystallised on adding cold water. 0·8 gram of crystals was thus obtained, which on recrystallisation from about 25 c.c. of boiling water yielded glistening plates, melting at 197°:

0·1702 gave 0·2928 CO_2 and 0·0805 H_2O. C=46·9; H=5·25.
0·2040 „ 13·2 c.c. N_2 (moist) at 16° and 756 mm. N=7·50.
0·2059 „ 13 c.c. N_2 „ „ 16° „ 757 mm. N=7·33.
0·1650 „ 0·0998 AgI. I=32·7.
$C_{15}H_{21}O_2N_2I$ requires C=46·4; H=5·4; N=7·2; I=32·7 per cent.

Unlike hypaphorine, the above base does not yield a sparingly soluble nitrate, but on warming for a few minutes on the water-bath with 1 per cent. aqueous sodium hydroxide, it is converted into hypaphorine; on acidification with nitric acid the nitrate of the latter base crystallises out. Conversely, on heating hypaphorine in methyl alcohol with sodium hydroxide and methyl iodide, the above-mentioned iodide of the ester is formed. The identity of the iodide from both sources was established by a melting-point determination of their mixture, and by solubility determinations:

100 grams of water at 18° dissolved 0·5015 gram of iodide from tryptophan.
100 grams of water at 18° dissolved 0·501 gram of iodide from hypaphorine.

Hypaphorine from the above Iodide.

By hydrolysis with sodium hydroxide, as described above, the iodide of the ester yielded hypaphorine, which was isolated as the nitrate. It is important to use only dilute alkali, for even then the odour of trimethylamine can be observed. On recrystallisation from hot water the nitrate melted somewhat indefinitely at 215—220°:

0·1112 gave 0·2230 CO_2 and 0·0618 H_2O. C=54·7; H=6·2.
$C_{14}H_{18}O_2N_2,HNO_3$ requires C=54·4; H=6·15 per cent.

The identity of the synthetic and the natural base was further established by a determination of the rotatory power of the former.

A solution of 0·299 gram of the nitrate, made up with ammonia and water to 18 c.c., gave, in a 2-dcm. tube, α_D +2·50° for

the base, whence $[\alpha]_D + 94.7°$. Greshoff found $[\alpha]_D$ 91—93° for the natural base.

The close relationship of hypaphorine to tryptophan is also expressed by several qualitative reactions; both substances have reducing properties, and, as already stated by Greshoff, hypaphorine reduces gold chloride, potassium permanganate, and ferric salts in the cold. A more characteristic and very delicate reaction which both substances have in common is that of Adamkiewicz, as modified by Hopkins and Cole, namely, an intense violet coloration on the addition of glyoxylic and sulphuric acids. On the other hand, a solution of hypaphorine is readily distinguished from a tryptophan solution by the fact that, since hypaphorine is not an amino-acid, it does not give Ruhemann's reaction with triketohydrindene hydrate (Trans., 1910, **97**, 1446; compare Abderhalden and Schmidt, *Zeitsch. physiol. Chem.*, 1911, **72**, 37).

In spite of similarity in structure, the oxidation of hypaphorine with ferric chloride proceeds quite differently from that of tryptophan. When treated according to Hopkins and Cole's method, the latter substance readily yields β-indolealdehyde, but in several experiments we could obtain from hypaphorine only a minute quantity of a substance, insufficient for complete identification. This substance, on sublimation under greatly diminished pressure, yielded crystals closely resembling those of β-indolealdehyde (similarly sublimed), but melting indefinitely about 10° lower. Oxidation experiments with hydrogen peroxide, with and without a ferrous salt as catalyst, were likewise unsuccessful.

The methylation of tryptophan also greatly changes the behaviour of the substance with sodium hydroxide, so that hypaphorine, unlike its parent substance, readily decomposes into indole and trimethylamine.

ORGANIC CHEMICAL LABORATORY, UNIVERSITY OF UTRECHT, HOLLAND.

CHEMICAL LABORATORY, GOLDSMITHS' COLLEGE, NEW CROSS, S.E.

CCXXXV.—*Dihydroxydihydrindamine and its Resolution into Optically Active Components.*

By WILLIAM JACKSON POPE and JOHN READ.

WHEN an externally compensated alkyl halogen compound condenses with ammonia to form a secondary amine the reaction may conceivably proceed in two distinct kinds of way. The resulting

secondary base may contain (1) two enantiomorphously similar alkyl groups, or (2) two enantiomorphously related alkyl groups; in case (1) the secondary amine would be externally compensated, and in case (2) it would be internally compensated. Apparently no reaction of this kind has been hitherto examined, although it is one of some little importance in connexion with the mode in which chemical change occurs between optically active substances. At first sight it might appear probable that, in the condensation referred to, both the externally compensated and the internally compensated secondary amine would be produced in approximately equal proportion; on the other hand, however, it is generally recognised that reaction between alkyl halogen compounds and ammonia is modified by steric hindrance, and it may be suggested as not impossible that steric hindrance might operate to different degrees as between two enantiomorphously similar and two enantiomorphously related molecules. If some modifying cause resembling steric hindrance were operative the externally compensated and the internally compensated secondary amine would be produced in different proportion.

For the purpose of elucidating this question we have examined the conversion of externally compensated bromohydroxyhydrindene,

$C_6H_4<{-CH_2-\atop CH(OH)}>CHBr$, into

$$C_6H_4<{-CH_2-\atop CH(OH)}>CH\cdot NH\cdot CH<{-CH_2-\atop CH(OH)}>C_6H_4,$$

the secondary amine, dihydroxydihydrindamine.

Experimental.

Externally Compensated Bromohydroxyhydrindene,

$$C_6H_4<{-CH_2-\atop CH(OH)}>CHBr.$$

This substance was prepared by Krämer and Spilker (*Ber.*, 1890, **23**, 3276) by the continued boiling of dibromohydrindene with dilute alcohol. This process being rather tedious and unsatisfactory, we have devised the following method for preparing bromohydroxyhydrindene, which rapidly furnishes a 70 per cent. yield of the pure substance.

Indene is well agitated with bromine water, which it immediately decolorises, and further quantities of bromine water are added until the colour is no longer discharged after prolonged shaking; in order to reduce the volume of aqueous solution used, the later quantities of bromine may be added in aqueous potassium bromide solution. The indene becomes converted into a pasty, white, crystalline mass, from which the aqueous solution is poured off, and which is then

treated with light petroleum; the latter solvent extracts the oily impurity, and leaves a colourless, hard, crystalline product. On evaporating the petroleum from the extract a heavy, brown oil remains, which on repeated boiling with successive quantities of water yields a further quantity of bromohydroxyhydrindene. After crystallisation from aqueous alcohol, the pure substance is obtained in long, colourless needles, melting at 128—129°; on spontaneous evaporation of its solution in ethyl acetate, it is deposited in colourless, pseudohexagonal crystals, of which Mr. Arthur Hutchinson, M.A., has kindly furnished the following description:

"Crystal system: monosymmetric—$a : b : c = 3{\cdot}2080 : 1 : 2{\cdot}4615$; $\beta = 60°0'$.

Forms observed: $a\{100\}$, $c\{001\}$, $x\{\bar{1}01\}$, $y\{\bar{2}01\}$, and $v\{\bar{1}11\}$.

The following angular measurements were obtained:

	Measured.	Calculated.
$ac = 100 : 001$	60° 0′	—
$cx = 001 : \bar{1}01$	47 4	47° 9
$cy = 001 : \bar{2}01$	79 59	80 4
$ay = \bar{1}00 : \bar{2}01$	39 56	—
$xv = \bar{1}01 : \bar{1}11$	66 58	—
$av = \bar{1}00 : \bar{1}11$	83 34	83 22

The crystals are doubly terminated prisms from 5 to 10 mm. long and from 1 to 3 mm. thick. They are elongated along the diad axis, and resemble in habit crystals of the mineral epidote. The prisms a, c, and y are always present, and usually equally developed. The faces x occur but seldom, and are very narrow. The only terminal planes observed are those belonging to the form v. There is a highly perfect cleavage parallel to $c\{001\}$, and a less perfect, somewhat fibrous, cleavage parallel to $a\{100\}$. The obtuse bisectrix coincides with the diad axis. The acute bisectrix is almost normal to $a\{100\}$, and a characteristic interference figure, showing strong horizontal dispersion and an axial angle in air of approximately 52°, can be seen through these faces."

It will be noted that in the production of bromohydroxyhydrindene from indene two carbon atoms in the molecule become asymmetric, so that the former substance should exist in two externally compensated modifications. The crystalline substance just described is, however, certainly uniform, and thus can only represent one of the two possible externally compensated isomerides. We have obtained no evidence of the formation of an isomeride during the above preparation, although it is, of course, quite possible that such an isomeride may be present in the oily material formed.

Hydroxyhydrindamine and Dihydroxydihydrindamine.

Hydroxyhydrindamine, $C_6H_4<\begin{smallmatrix}-CH_2-\\CH(OH)\end{smallmatrix}>CH \cdot NH_2$, and dihydroxydihydrindamine, $\left(C_6H_4<\begin{smallmatrix}-CH_2-\\CH(OH)\end{smallmatrix}>CH\right)_2NH$, were prepared by Spilker (*Ber.*, 1893, **26**, 1542) by treating bromohydroxyhydrindene with alcoholic ammonia in the cold. This method is, however, conveniently replaced by the following process for preparing the two substances.

Bromohydroxyhydrindene (200 grams) is shaken mechanically in a stoppered Winchester bottle with ammonia (D 0·880; 800 grams); a clear solution first results, and this soon begins to deposit the secondary amine. After agitation for about two days the product is exposed in open basins until most of the ammonia has volatilised; the crude secondary base is then collected, and well washed with cold water. The filtrate and the washings are preserved, to be worked up for the preparation of the primary amine, which they contain in the form of hydrobromide.

Externally Compensated Dihydroxydihydrindamine,

$$C_6H_4<\begin{smallmatrix}-CH_2-\\CH(OH)\end{smallmatrix}>CH \cdot NH \cdot CH<\begin{smallmatrix}-CH_2-\\CH(OH)\end{smallmatrix}>C_6H_4.$$

The crude secondary amine (70 grams), prepared as above described, melts at about 160°; it is dissolved in hydrochloric acid, precipitated with ammonia, and then, after collection, crystallised from alcohol. The several fractions obtained in this way consist of small, white, feathery needles, and melt rather indefinitely at about 183°; they evidently represent the substance obtained by Spilker (*loc. cit.*), which melted at 186°.

On repeatedly extracting the substance melting at 183° with boiling ethyl acetate and recrystallising the sparingly soluble residue from boiling alcohol, a product is obtained which crystallises in small, glistening needles, and melts at 205°. This substance constitutes by far the larger proportion of the whole crude secondary amine; it is consequently to be concluded that the secondary amine now described melts at 205°, but, in the crude condition, is contaminated with some other substance which is not easily removed by recrystallisation, and which depresses the melting of the amine.

Dihydroxydihydrindamine d-*Camphor-β-sulphonate.*

The method just above indicated for preparing the pure externally compensated dihydroxydihydrindamine by extraction with ethyl

acetate and crystallisation of the residue from alcohol is inconvenient, and furnishes a very poor yield of the pure substance; the following process is much more satisfactory. The crude secondary amine melting at about 183° is dissolved in an alcoholic solution of the equivalent amount of *d*-camphor-β-sulphonic acid, and the alcoholic solution evaporated until crystallisation occurs. The white, crystalline mass of fine needles thus obtained is further purified by crystallisation from hot water, and then treated with ammonia to liberate the base; the secondary amine thus obtained is the pure externally compensated substance, melting at 205°.

ddll-*Dihydroxydihydrindamine Platinichloride.*

The externally compensated base melting at 205° yields the platinichloride when treated with platinic chloride in hydrochloric acid solution; this substance separates from hot water in glistening, orange-yellow scales, melting at 211°. It is sparingly soluble in cold water, and dissolves readily in alcohol:

0·2739 gave 0·0548 Pt. Pt = 20·01.

$C_{36}H_{38}O_4N_2,H_2PtCl_6$ requires Pt = 20·08 per cent.

Attempts to obtain the Internally Compensated or dl-*Dihydroxydihydrindamine.*

The mother liquors obtained from the separation of the above-described *d*-camphor-β-sulphonate and from the ethyl acetate treatment of the original crude dihydroxydihydrindamine yield on prolonged fractional crystallisation a small proportion of a substance which is more soluble in the usual solvents than the secondary amine melting at 205°. It crystallises in colourless needles, and melts fairly sharply at 178°. The following analysis was made:

0·0862 gave 0·2431 CO_2 and 0·0543 H_2O. C = 76·91; H = 7·05.

$C_{18}H_{19}O_2N$ requires C = 76·82; H = 6·81 per cent.

The platinichloride of this substance was obtained as a yellow oil, which could not be caused to solidify.

From the facts described above it appears legitimate to conclude that the externally compensated secondary base melting at 205° is accompanied by a small proportion of the internally compensated isomeride, and that the latter melts at about 178°.

The Resolution of Externally Compensated Dihydroxydihydrindamine.

It has been shown above that on crystallising dihydroxydihydrindamine with *d*-camphor-β-sulphonic acid a partly racemic salt is formed, and that no resolution of the externally compensated base

can be effected by crystallisation with the optically active acid under ordinary conditions.

On crystallising the secondary amine melting at about 183° from an aqueous solution of the corresponding amount of *d*-α-bromocamphor-π-sulphonic acid, a partly crystalline mass is deposited which, after separation, is obtained in small, opaque nodules by crystallisation from hot water; the salt is very difficult to purify, owing mainly to the ease with which hydrolytic dissociation occurs, but the purification is facilitated by crystallisation from boiling ethyl acetate containing a little alcohol. The salt ultimately obtained yields, when treated with ammonia, the dextro-amine contaminated with some amount of the lævo-isomeride.

By prolonged fractional crystallisation of the crude bromocamphorsulphonate from ethyl acetate, it can be resolved into the sparingly soluble *d*-dihydroxydihydrindamine *d*-α-bromocamphor-π-sulphonate and the more readily soluble *l*-dihydroxydihydrindamine *d*-α-bromocamphor-π-sulphonate. The difference in solubility between these two salts is, however, so slight that no large proportion of the two active secondary amines can be separated in the form of the pure salts. It is most convenient to effect a rough separation by allowing about two-thirds of the salt to crystallise from ethyl acetate, and then to liberate the crude *d*-base from the sparingly soluble salt, and the crude *l*-isomeride from the mother liquors by treatment with ammonia; the optically active secondary amines are much less soluble in alcohol than is the externally compensated isomeride, and the former may easily be obtained in a state of purity by crystallising the crude bases from this solvent; thus, in one case, the mother liquors yielded a base exhibiting the specific rotatory power, $[\alpha]_{Hg\,green}$ $-52\cdot6°$; after one crystallisation from alcohol this value was found to be $-95\cdot7°$, and a second crystallisation raised the specific rotatory power to that of the pure *l*-amine, namely, $-100\cdot0°$.

d *and* l-*Dihydroxydihydrindamine*,

$$\left[C_6H_4{<}{\substack{CH_2\\CH(OH)}}{>}CH\right]_2NH.$$

The *d*- and *l*-dihydroxydihydrindamines are sparingly soluble in boiling alcohol, and separate therefrom in long, silky needles, melting at 223°; on crystallising equal quantities of the two isomerides together from alcohol, the externally compensated substance melting at 205° is obtained. This completes the proof that the compound described above (p. 2074) is the pure externally compensated secondary base:

0·0888 of *l*-base gave 0·2503 CO_2 and 0·0556 H_2O. C=76·87; H=7·01.

$C_{18}H_{19}O_2N$ requires C=76·82; H=6·81 per cent.

The very sparing solubility of these bases in the ordinary solvents renders it difficult to determine their rotation constants in neutral solvents; further, the substances are so feebly basic that their salts are hydrolytically dissociated with great readiness, and it is consequently difficult to ensure the purity of the solid salts. The following determinations of rotatory power were therefore made by dissolving known weights of the bases in the calculated quantities of hydrochloric acid, making up to 30·0 c.c. with water, and examining at 18° in 4-dcm. tubes.

l-*Dihydroxydihydrindamine.*

Weight taken.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
0·0990 gram	α	− 1·32°	− 1·14°	− 1·10°
	[α]	100·0	86·4	83·3
	[M]	281·0	243·0	234·0
0·6022 gram	α	7·88	6·78	6·53
	[α]	98·1	84·4	81·3
	[M]	276·0	237·0	229·0

d-*Dihydroxydihydrindamine.*

0·1037 gram	α	+ 1·38°	+ 1·19°	+ 1·15°
	[α]	99·8	86·1	83·2
	[M]	281·0	242·0	234·0

The mean rotatory dispersions for the basic ion in aqueous solution are thus, for Hg_{green}/Na_{yellow} = 1·200, and for Hg_{yellow}/Na_{yellow} = 1·037.

d- *and* l-*Dihydroxydihydrindamine Platinichloride,* $[(C_9H_9O)_2NH]_2,H_2PtCl_6$.

The platinichlorides of the active bases separate from hot water, in which they are moderately soluble, in glistening, orange needles, melting at 185°; the solutions must be kept slightly acidified with hydrochloric acid in order to prevent precipitation of the base owing to hydrolytic dissociation. The salts are readily soluble in alcohol:

0·3013 gave 0·0602 Pt. Pt=19·98.

$C_{36}H_{38}O_4N_2,H_2PtCl_6$ requires Pt=20·08 per cent.

The following determinations of rotatory powers were made by dissolving 0·1508 gram of *d*-hydroxydihydrindamine platinichloride

in water with addition of a drop of dilute hydrochloric acid, making up to 30 c.c. with water, and examining in a 4-dcm.-tube at 18°.

	Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
α	+ 1·12°	+ 0·95°	+ 0·93°
$[\alpha]$	55·7	47·2	46·3
$[M]/2$	271·0	230·0	225·0

The rotatory dispersions are, for $Hg_{green}/Na_{yellow} = 1·203$, and for $Hg_{yellow}/Na_{yellow} = 1·019$. These values are in good agreement with those quoted above for the basic ions in hydrochloric acid solution.

l-*Dihydroxydihydrindamine* d-*α-Bromocamphor-π-sulphonate*, $(C_9H_9O)_2NH,C_{10}H_{14}OBr·SO_3H,H_2O$.

This salt is conveniently obtained in a state of high purity by crystallising the *l*-base with the corresponding amount of the *d*-acid from water, and recrystallising the product from water slightly acidified with hydrochloric acid; it forms opaque clusters of minute colourless needles, melting at 210—215°:

0·0953 gave 0·1884 CO_2 and 0·0512 H_2O. C = 55·07; H = 6·14.

$C_{28}H_{36}O_7NBrS$ requires C = 55·08; H = 5·95 per cent.

0·2731 lost 0·0078 at 100°. $H_2O = 2·86$; $1H_2O$ requires 2·95.

The following determinations of rotatory power were made with the air-dried salt (1) in alcoholic solution, and (2) in water, with the addition of a drop of dilute hydrochloric acid; the weight taken was made up to 30 c.c., and the solution examined in a 4-dcm. tube at 18°.

Weight taken.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
0·1522 gram	α	+ 0·88°	+ 0·74°	+ 0·69°
in alcohol	$[\alpha]$	43·4	36·5	34·0
	$[M]$	265·0	223·0	207·0

Rotatory dispersions: $Hg_{green}/Na_{yellow} = 1·276$; $Hg_{yellow}/Na_{yellow} = 1·074$.

0·1020 gram	α	+ 0·13°	+ 0·09°	+ 0·08°
in water	$[\alpha]$	9·6	6·6	5·9
	$[M]$	59·0	40·0	36·0
Calculated ...	$[M]$	65·4	52·3	44·5

Rotatory dispersions: $Hg_{green}/Na_{yellow} = 1·627$; $Hg_{yellow}/Na_{yellow} = 1·119$. The calculated values for the molecular rotatory powers are derived from the values observed for the hydrochloric acid solutions of the base and of aqueous solutions of the ammonium salt of the acid; the observed values are low, probably owing to the presence of a slight excess of the base produced by hydrolytic dissociation.

l-Dihydroxydihydrindamine l-a-Bromocamphor-π-sulphonate.

This salt is prepared in a state of purity in the same manner as the one previously described; it forms long, silky, colourless needles, melting at 230—232°, and is easily soluble in alcohol or ethyl acetate, and sparingly so in water:

0·0976 gave 0·1959 CO_2 and 0·0530 H_2O. C=54·71; H=6·08.

$C_{28}H_{36}O_7NBrS$ requires C=55·05; H=5·95 per cent.

0·2360 lost 0·0071 at 100°. H_2O=3·01; $1H_2O$ requires 2·95.

The following determinations of rotatory power were made in the same way as those quoted for the previous salt:

Weight taken.		Hg_{green}.	Hg_{yellow}.	Na_{yellow}.
0·1525 gram	α	− 1·69°	− 1·41°	− 1·34°
in alcohol	[α]	83·1	69·3	65·9
	[M]	507·0	423·0	402·0

Rotatory dispersions: Hg_{green}/Na_{yellow} = 1·261; Hg_{yellow}/Na_{yellow} = 1·052.

0·1000 gram	α	− 1·37°	− 1·18°	− 1·10°
in water	[α]	102·8	88·5	82·5
	[M]	628·0	540·0	503·0
Calculated......	[M]	628·0	538·0	513·0

Rotatory dispersions: Hg_{green}/Na_{yellow} = 1·246; Hg_{yellow}/Na_{yellow} = 1·073. The calculated values for the molecular rotatory powers were derived in the manner indicated for the previously described salt.

Externally Compensated Hydroxyhydrindamine,

$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH\cdot NH_2.$$

In order to obtain this primary amine it is convenient to evaporate the aqueous mother liquors containing the hydrobromide, referred to on p. 2074, to dryness on the water-bath, then to dissolve in a little boiling water, and to add about twice the calculated quantity of concentrated aqueous potassium hydroxide after partial cooling. The crude amine separates as a pale yellow, crystalline precipitate, and is obtained in a state of purity by crystallisation from boiling benzene; it forms glistening, white scales, melting at 128—129°, and is quite stable in the air. It does not appear to absorb carbon dioxide and moisture from the atmosphere in the manner mentioned by Spilker (*loc. cit.*). The hydrochloride is precipitated from concentrated solutions by excess of hydrochloric acid as a white, crystalline mass; the *platinichloride* crystallises from hot water in orange needles, melting at 232°, and is readily soluble in alcohol:

0·3067 gave 0·0845 Pt. Pt=27·55.

$C_{18}H_{22}O_2N_2,H_2PtCl_6$ requires Pt=27·56 per cent.

The resolution of this amine into its optically active components can be effected by crystallisation with *d*-α-bromocamphor-π-sulphonic acid, and will shortly be described.

In the treatment of externally compensated bromohydroxyhydrindene with concentrated aqueous ammonia solution in the manner described above, it is converted quantitatively into a mixture of the secondary base and the primary base, hydroxyhydrindamine; in one large preparation the former product was obtained in a 55 per cent. yield, and the primary amine in a 45 per cent. yield, no unchanged material being recovered.

It is to be supposed that the first action of the ammonia is to convert bromohydroxyhydrindene into the primary externally compensated amine, hydroxyhydrindamine, and that by the action of bromohydroxyhydrindene the latter substance becomes partly converted into the secondary dihydroxydihydrindamine. We have shown that the secondary amine melting at 183° consists mainly of the externally compensated base melting at 205°, and contains but a small proportion of an isomeride melting at 178°, this being probably the internally compensated secondary amine; it therefore follows that in the formation of the secondary base condensation occurs between the alkyl bromide and hydroxyhydrindamine, which are enantiomorphously similar in molecular configuration, and that very little tendency is exhibited for condensation to occur between the hydroxyhydrindyl radicles of enantiomorphously dissimilar configurations. Representing the hydroxyhydrindyl radicle,

$$C_6H_4<\begin{matrix}CH_2\\CH(OH)\end{matrix}>CH,$$

by the symbol R, the reaction which occurs to a preponderating extent is represented by the equations:

$$d\text{-R}\cdot NH_2 + d\text{-RBr} = (d\text{-R})_2NH + HBr$$

and

$$l\text{-R}\cdot NH_2 + l\text{-RBr} = (l\text{-R})_2NH + HBr.$$

The alternative reactions represented by the equations:

$$d\text{-R}\cdot NH_2 + l\text{-RBr} = (d\text{-R})(l\text{-R})NH + HBr$$

and

$$l\text{-R}\cdot NH_2 + d\text{-RBr} = (d\text{-R})(l\text{-R})NH + HBr$$

apparently proceed to but a very slight extent.

THE CHEMICAL LABORATORY,
THE UNIVERSITY, CAMBRIDGE.

CCXXXVI.—*Studies in Phototropy and Thermotropy. Part II. Naphthylideneamines.*

By ALFRED SENIER and ROSALIND CLARKE.

r previous communications on certain Schiff's bases (Senier and epheard, Trans., 1909, **95**, 441, 1943) several of these compounds re described, some of which possessed phototropic properties, and arly all of which were thermotropic. It was noticed that those hibiting phototropy were all derived from salicylaldehyde, in hich the substituents are in the ortho-position with respect to ch other. Moreover, other investigators have shown generally at when isomerism occurs among Schiff's bases the compounds are tho-compounds, with a few exceptions, when they are para-. This ing so, it seemed interesting to continue the search for photo- opy and thermotropy among compounds of this class, and, for is purpose, we have prepared and studied a number of new bases erived from 2-hydroxy-α-naphthaldehyde, in which the naphthalene ucleus takes the place of the benzene ring in salicylaldehyde. one of the bases described proved to be phototropic, but all show ermotropy in greater or less degree. At the "lower tempera- ure" (*loc. cit.*) all become paler in colour, and at the "higher mperature" deeper; orange becomes yellow, and yellow, orange, r, in the case of the aminophenol derivatives, red.

The bases, naphthylideneamines, were prepared by bringing gether molecular proportions of the aldehyde and amine in coholic solution, and recrystallising the crystals thus obtained om that medium or from methyl alcohol.

2-Hydroxy-α-naphthylidene-o-chloroaniline,

$$OH\cdot C_{10}H_6\cdot CH{:}N\cdot C_6H_4Cl,$$

rystallises from alcohol in yellow needles, which are sparingly luble in ether, but readily so in acetone, chloroform, or light etroleum. It melts at 144·5° (corr.):

0·4860 gave 21·0 c.c. N_2 (moist) at 15° and 733 mm. N=4·88.

$C_{17}H_{12}ONCl$ requires N=4·97 per cent.

*2-Hydroxy-α-naphthylidene-*m*-chloroaniline,*

$$OH\cdot C_{10}H_6\cdot CH{:}N\cdot C_6H_4Cl,$$

curs in orange-yellow needles when crystallised from alcohol or ght petroleum. It is sparingly soluble in ether, readily so in nzene, chloroform, or acetone, and melts at 116—117° (corr.):

0·5222 gave 23·7 c.c. N_2 (moist) at 16·5° and 748 mm. N=5·20.

$C_{17}H_{12}ONCl$ requires N=4·97 per cent.

2-Hydroxy-a-naphthylidene-p-chloroaniline,

$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4Cl$,

consists of yellow, silky needles, which dissolve sparingly in ether, but are readily soluble in chloroform, acetone, benzene, or light petroleum. It melts at 158—159° (corr.):

0·5558 gave 23·4 c.c. N_2 (moist) at 14° and 766 mm. N = 4·99.
$C_{17}H_{12}ONCl$ requires N = 4·97 per cent.

2-Hydroxy-a-naphthylidene-o-bromoaniline,

$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4Br$,

was obtained in yellow needles, which dissolve readily in the usual solvents. It melts at 150° (corr.):

0·5546 gave 19·9 c.c. N_2 (moist) at 14° and 780 mm. N = 4·33.
$C_{17}H_{12}ONBr$ requires N = 4·30 per cent.

2-Hydroxy-a-naphthylidene-m-bromoaniline,

$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4Br$,

crystallises in orange-yellow needles. Its behaviour towards the usual solvents is similar to that of the ortho-compound. It melts at 144° (corr.):

0·5016 gave 17·8 c.c. N_2 (moist) at 13·5° and 778 mm. N = 4·2[illegible]
$C_{17}H_{12}ONBr$ requires N = 4·30 per cent.

2-Hydroxy-a-naphthylidene-p-bromoaniline,

$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4Br$,

separates, in the first instance, in yellow leaflets, and, when recrystallised from alcohol, in pale yellow, silky needles. It dissolves readily in benzene, chloroform, acetone, or light petroleum, and less so in ether. It melts at 166·5° (corr.):

0·4930 gave 17·7 c.c. N_2 (moist) at 13° and 769 mm. N = 4·30.
$C_{17}H_{12}ONBr$ requires N = 4·30 per cent.

2-Hydroxy-a-naphthylidene-m-nitroaniline,

$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}NO_2$,

occurs in orange-red needles. It dissolves readily in alcohol, benzene, or chloroform, more sparingly in light petroleum, and melts at 178·5—179·5° (corr.):

0·3331 gave 27 0 c.c. N_2 (moist) at 17° and 772 mm. N = 9·5[illegible]
$C_{17}H_{12}O_3N_2$ requires N = 9·59 per cent.

2-Hydroxy-a-naphthylidene-o-aminophenol,

$OH{\cdot}C_{10}H_6{\cdot}CH{:}N{\cdot}C_6H_4{\cdot}OH$,

separates in brown crystals, which are somewhat soluble in the usual solvents, but do not readily crystallise from them. It melts and decomposes at 248—250° (corr.):

0·4777 gave 22·2 c.c. N_2 (moist) at 19° and 765 mm. N = 5·3[illegible]
$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

2-Hydroxy-α-naphthylidene-m-*aminophenol*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OH,$$

eparated in yellow needles, which were recrystallised from alcohol. t dissolves readily in most solvents, with the exception of light etroleum, in which it is almost insoluble. It begins to melt and lecompose at 221° (corr.):

0·4334 gave 19·4 c.c. N_2 (moist) at 22° and 765 mm. N = 5·11.
$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

2-Hydroxy-α-naphthylidene-p-*aminophenol*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OH,$$

t first appeared as yellow needles, which became darker on successive recrystallisations from alcohol. It melts and decomposes at 229·5° (corr.):

0·5584 gave 26·3 c.c. N_2 (moist) at 15° and 750 mm. N = 5·65.
$C_{17}H_{13}O_2N$ requires N = 5·32 per cent.

2-Hydroxy-α-naphthylidene-o-*anisidine*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OMe,$$

ccurs as bright yellow, silky crystals, which dissolve readily in the usual solvents. It melts at 178·5° (corr.):

0·5543 gave 23·8 c.c. N_2 (moist) at 9° and 779 mm. N = 5·29.
$C_{18}H_{15}O_2N$ requires N = 5·05 per cent.

2-Hydroxy-α-naphthylidene-m-*anisidine*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OMe,$$

orms yellow needles, which dissolve readily in the usual solvents, nd melt at 107·5—108·5 (corr.):

0·4468 gave 19·3 c.c. N_2 (moist) at 17° and 762 mm. N = 5·03.
$C_{18}H_{15}O_2N$ requires N = 5·05 per cent.

2-Hydroxy-α-naphthylidene-p-*anisidine*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot OMe,$$

rystallises in clusters of long, yellow, silky needles, which are eadily soluble in the usual solvents, and melt at 111—112° (corr.):

0·4798 gave 20·3 c.c. N_2 (moist) at 11·5° and 766 mm. N = 5·08.
$C_{18}H_{15}O_2N$ requires N = 5·05 per cent.

2-Hydroxy-α-naphthylidene-o-*aminobenzoic acid*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

separated in orange-yellow crystals. It is sparingly soluble in methyl alcohol, more readily so in benzene, ethyl acetate, chloroform, toluene, or light petroleum, and melts at 227·5° (corr.):

0·5014 gave 20·8 c.c. N_2 (moist) at 20° and 766 mm. N = 4·78.
$C_{18}H_{13}O_3N$ requires N = 4·81 per cent.

2-Hydroxy-α-naphthylidene-m-*aminobenzoic acid*,

$$OH\cdot C_{10}H_6\cdot CH:N\cdot C_6H_4\cdot CO_2H,$$

occurs in yellow needles, which are sparingly soluble in benzene or light petroleum, but readily so in alcohol or chloroform. It melts and decomposes at 281·5° (corr.):

0·3417 gave 14·0 c.c. N_2 (moist) at 19° and 767 mm. N = 4·76.
$C_{18}H_{13}O_3N$ requires N = 4·81 per cent.

2-Hydroxy-α-naphthylidene-p-*aminobenzoic acid*,
$OH \cdot C_{10}H_6 \cdot CH{:}N \cdot C_6H_4 \cdot CO_2H$,
separates in yellow crystals, which are sparingly soluble in alcohol, more readily so in chloroform, benzene, or methyl alcohol, and insoluble in light petroleum. It melts and decomposes at 29[illegible] (corr.):

0·4621 gave 19·2 c.c. N_2 (moist) at 27° and 771 mm. N = 4·67.
$C_{18}H_{13}O_3N$ requires N = 4·81 per cent.

2-Hydroxy-α-naphthylidene-o-4-xylidine,
$OH \cdot C_{10}H_6 \cdot CH{:}N \cdot C_6H_3Me_2$,
crystallises in yellow needles, dissolves readily in the usual solvents, and melts at 125·5° (corr.):

0·5746 gave 24·0 c.c. N_2 (moist) at 10° and 763 mm. N = 5·02.
$C_{19}H_{17}ON$ requires N = 5·09 per cent.

2-Hydroxy-α-naphthylidene-m-*4-xylidine*,
$OH \cdot C_{10}H_6 \cdot CH{:}N \cdot C_6H_3Me_2$,
forms yellow needles, melting at 157° (corr.). Its behaviour towards solvents is similar to that of the ortho-compound:

0·4637 gave 19·8 c.c. N_2 (moist) at 15·5° and 762 mm. N = 5·01.
$C_{19}H_{17}ON$ requires N = 5·09 per cent.

2-Hydroxy-α-naphthylidene-p-*xylidine*,
$OH \cdot C_{10}H_6 \cdot CH{:}N \cdot C_6H_3Me_2$,
was obtained in yellow crystals, which dissolve in the usual solvents. It melts at 108·5—109·5° (corr.):

0·4874 gave 21·1 c.c. N_2 (moist) at 18° and 750 mm. N = 4·94.
$C_{19}H_{17}ON$ requires N = 5·09 per cent.

2-Hydroxy-α-naphthylidene-ψ-cumidine,
$OH \cdot C_{10}H_6 \cdot CH{:}N \cdot C_6H_2Me_3$,
separates in yellow needles, which are readily soluble in alcohol, chloroform, benzene, or light petroleum, and melt at 146—147° (corr.):

0·5996 gave 25·2 c.c. N_2 (moist) at 15° and 759 mm. N = 4·92.
$C_{20}H_{19}ON$ requires N = 4·84 per cent.

UNIVERSITY COLLEGE,
GALWAY.

CCXXXVII.—*Isomeric Acetaldehydephenylhydrazones.*

By Ernyst Graham Laws and Nevil Vincent Sidgwick.

After preliminary work by Emil Fischer, and Bamberger and Pemsel, the isomeric acetaldehydephenylhydrazones were carefully investigated by Lockemann and Liesche (*Annalen*, 1905, **342**, 14), who showed that the α-form was converted into the β- by acids, and that the β- was transformed into the α-modification by alkalis, and, further, that it was not necessary for the hydrazone to pass into solution in the course of these transformations. These results are quite exceptional, and it was thought worth while to re-investigate these substances.

Experimental.

Preparation of the Hydrazone.

Lockemann and Liesche prepared the hydrazone in light petroleum solution, but a purer yield is obtained by using aqueous alcohol as solvent. One hundred and twenty c.c. of alcohol were mixed with 20 c.c. of water in a flask fitted with cork and upright condenser, and placed in a trough of cold water. Thirty grams of acetaldehyde were poured in, and the mixture shaken. Sixty grams of phenylhydrazine, purified by recent distillation in a vacuum, were then added in portions, the whole being shaken after each addition, and time being given to cool before adding the next. (If the mixture becomes hot, decomposition sets in, and the preparation is ruined.) Crystallisation can be induced by sowing or scratching, and the liquid should be shaken until small crystals are distributed throughout the whole mass. The apparatus is left for an hour or so to cool completely. The material is then collected, and washed with a little aqueous alcohol. The product is pure white, and does not become discoloured in air for some time. In one experiment, using the above quantities, the product when dry weighed 56 grams.

The hydrazone obtained in this way had in different experiments melting points varying between 56° and 80°, the value depending no doubt on the relative proportions of the two isomerides present. The hydrazone decomposes in air, very slowly at first, but afterwards more rapidly, becoming finally a dark brown oil. It is best stored in a vacuum over potassium hydroxide or phosphoric oxide.

Preparation of the Isomerides.

α-Form.—After recrystallisation from aqueous alcohol containing a trace of potassium hydroxide, the product invariably had a high

melting point—from 80° to 98°—the figures depending partly no doubt on the purity of the product. The highest values were obtained when the hydrazone was prepared from phenylhydrazine which had been freshly distilled, or when the product was distilled in a vacuum previous to crystallisation from alkaline alcohol; then the melting point was always above 93°, and generally 98°. This effect was always produced by a single crystallisation. The temperature to which the liquid was heated before cooling, or the time for which the heating was continued, seemed to have no effect on the transformation. The concentration of the alkali was not important provided that sufficient was present to make the liquid definitely alkaline.

β-Form.—Recrystallisation of the product from aqueous alcohol containing a trace of sulphur dioxide gave, as Lockemann and Liesche state, the β-form, melting at 56°. Great care is necessary here, for if the concentration of the acid is too great, or if the solution is heated to too high a temperature or for too long a time, decomposition sets in, and nothing can be induced to crystallise out. The solution must remain straw-coloured; if it becomes definitely yellow the preparation is spoilt. The stronger acids were found by Lockemann and Liesche to be unsuited for the purpose—an impure product was always obtained owing to decomposition. If, however, the stronger acids are used at great dilution, a pure product, melting sharply at 56°, is always obtained. Rapid recrystallisation from 75 per cent. aqueous alcohol containing two to three drops of hydrochloric acid was the method generally adopted for the preparation of the β-form.

Transformation of the Isomerides.

By recrystallisation from acidic aqueous alcohol, by immersion in aqueous acids, and by leaving the solid in an atmosphere of sulphur dioxide, the α-form (m. p. 98°) and products of intermediate melting point are converted into the β-form (m. p. 56°).

By recrystallisation from alkaline aqueous alcohol, by immersion in aqueous alkalis, and by keeping in an atmosphere of ammonia gas, the melting point of the β-form is raised considerably, although this reverse change does not always proceed sufficiently to give the pure α-product melting at 98°.

These experiments confirmed the most important points in Lockemann and Liesche's paper. In particular, it was noted that where the transformation was caused by aqueous and gaseous alkali or acid, the crystals were quite unaltered during the process, and no change in their appearance could be detected even under the microscope. The action of alkalis takes place much more slowly and often less completely than the opposite action of acids. Drying with

hosphoric oxide greatly retards the change in the case of sulphur ioxide, but drying with potassium hydroxide seems to be without fect on the action of ammonia in causing the reverse transforma-on.

Effect of Fusion.

Experiments in which each form was kept fused in a vacuum howed that the freezing point had not undergone any appreciable hange after one hour. After six hours the freezing point of the form, originally 98°, had fallen to 90°, whilst that of the β-form, riginally 56°, had fallen to 55°, but it was noticed that both liquids ad now become discoloured.

On fusion in air the fall in freezing point and the darkening of the liquid occurred more quickly, for example, the α-form, originally fusing at 98°, melted at 55° after three hours. Working rapidly in air, two successive freezing points could be obtained with the same portion of material not differing by more than 1°.

These experiments seemed to indicate that the freezing point did not change until decomposition set in, as indicated by the darkening of the liquid.

Freezing-point Curve.—Various difficulties, due probably to the ow heat of fusion of the hydrazone and to its small velocity of crystallisation, were encountered in the attempts to obtain this curve. The method finally adopted was as follows:

The mixture of α- and β-forms was made up in the required proportions in the substance tube of a Beckmann apparatus, fused completely at as low a temperature as possible, and at once withdrawn and allowed to cool in the air until crystallisation occurred. It was always stirred vigorously, so that very fine crystals were produced. The tube was then placed in position in the Beckmann apparatus, and the bath, previously regulated to a few degrees below the expected freezing point, gently heated. The substance soon became warm and more liquid. The temperature at which the last few crystals disappeared was taken. It could be determined quite accurately, for the temperature rose very slowly until all the substance had liquefied, when the rate became much greater. The solid present made the mercury in the thermometer bulb appear quite dull, but, as the last crystals dissolved, the lustre of the mercury again became visible.

This temperature is not a freezing point in the ordinary sense of the word, but a "dissolving point." The method gives the temperature at which the crystals of highest melting point dissolve in the liquid with which they are in contact. Theoretically, it should be identical with the freezing point; practically, it will tend to be above the "theoretical freezing point" (when supercooling is

nil), whereas the ordinarily determined freezing point tends to be below it.

The results obtained by this method are given in the table below:

α-Form (grams).	β-Form (grams).	α-Form, per cent.	F. p.
		Set 1.	
6·0	0·0	100	98·6°
4·5	0·5	90	92·0
3·0	1·0	75	82·2
3·0	2·0	60	75·0
2·7	3·3	45	68·0
2·0	3·0	40	56·0 *
		Set 2.	
0·0	5·0	0	56·0°
0·9	5·1	15	59·0
1·5	3·5	30	63·2
2·0	3·0	40	65·4
2·5	2·5	50	69·8
2·0	1·0	66·6	78·0
		Set 3.	
0·0	5·0	0	56·0°
0·25	4·75	5	56·8
0·5	4·5	10	57·6
1·0	4·0	20	60·0

* Inexplicable except assuming that a trace of acid was accidentally introduced.

The three sets of experiments were carried out with different preparations of the isomerides. The results are also recorded in the curve on p. 2089.

This curve indicates that the two components—the two isomerides—form a continuous series of mixed crystals (solid solutions). The curve would necessarily fall at both ends if solid solutions were not formed. So far as is known, this is the first case where this has been established, although a similar behaviour has been assumed by Hantzsch in the case of the diazonium salts and nitrophenols. The behaviour in question is due to the close similarity in properties of the two forms, which is evident from the following considerations:

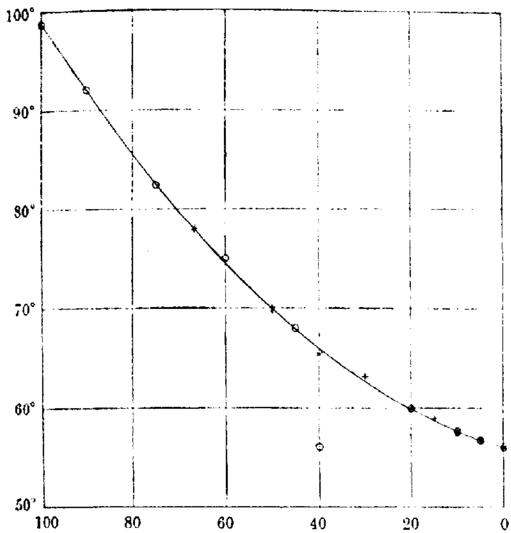
Some of the pure α- and β-forms, and also crystals of various intermediate melting points, were examined under the microscope. Irregularities in the crystals prevented exact measurements being taken, but, so far as they could be tested, they appeared to be absolutely identical. Moreover, no change could be seen, even in optical properties, while a fairly large crystal of α was being converted into β under the microscope by a drop of acid.

Again, the introduction of either isomeride will effect crystallisation of the other from its supersaturated solutions; thus crystals of the α-form when introduced into a supersaturated acid solution

of the hydrazone immediately cause the crystallisation of the β-variety, and, in the same way, the introduction of the β crystals causes the α-variety to separate out from alkaline solutions. From neutral solutions, crystals of intermediate melting point are obtained by sowing with α or β, and the melting point of the product is the same whichever be used.

Further, so far as could be determined, the two isomerides have

Freezing-point curve.



the same density, that of the α-form being 1·181, of the β-form 1·180, and of the mixed crystals 1·180.

Influence of the Solvent.

Lockemann and Liesche's conclusions on this question were not at all satisfactory. The method finally adopted in the present work was to recrystallise a fairly large quantity of each isomeride several times from each of the solvents investigated. The recrystallisations were done as rapidly as possible, and a fresh portion of solvent was used for each crystallisation, as hot solutions of the hydrazone soon begin to decompose when in contact with air. A sample of the hydrazone was reserved at each stage, and its freezing point determined by the method used in obtaining the above curve.

Solvent: Alcohol.

Form.	Original f.p.	Freezing point after recrystallising. Once.	Twice.	Thrice.	Four times.
α	98°	83·0°	77·2°	73·2°	7[illegible]
β	56	58·0	74·0	76·0	
mixed crystals	72	77·2	75·2	73·5	—
,,	68	73·6	76·4	75·0	—
,,	65	75·3	73·3	75·2	—

In each case there is a marked alteration on the first crystallisation, and then the freezing point oscillates between 73° and 77°. If the same portion of alcohol be used for the successive crystallisations, the freezing point of the α-form falls successively lower each time, whilst that of the β-form rises at first but finally falls. This behaviour is explained by the fact that a solution of the hydrazone in aqueous alcohol gradually becomes slightly acid on exposure to air. The "equilibrium values" obtained for alcohol are probably all too low, and their divergence is doubtless due to the varying amounts of acid produced in the process of each crystallisation. The experiments show that an equilibrium is reached in alcohol, but they do not indicate with certainty the value of that equilibrium.

Solvents: Benzene and Light Petroleum.—With each of these solvents the α- and β-forms remained unchanged in freezing point after three recrystallisations carried out in the above manner. Various mixtures, originally melting at points between 60° and 84°, finally gave an "equilibrium" product fusing between 82° and 83°.

Solvent: Water.

Form.	Original f.p.	Freezing point after crystallising. Once.	Twice.
α	98°	81·0°	81°
β	56	80·0	81
mixed crystals	75	81·0	81
,,	71	81·5	81

Water free from air was used in these experiments, as otherwise considerable oxidation occurred. These figures indicate that the isomeric change occurs rapidly in aqueous solutions, a definite equilibrium being established in the time required for a single crystallisation.

The hydrazone was found to be volatile in steam. Steam distillation gave exactly the same results as recrystallisation from water. Whatever the freezing point of the crystals used, the product invariably had a freezing point of 80—81°.

Vacuum Distillation.

Lockemann and Liesche state that each form can be distilled in vacuum, but give no details. In the following experiments the pressure was kept fairly constant at 20—21 mm.

β-Form.

	1st Fraction.		2nd Fraction.		3rd Fraction.	
Expt.	Collected at	Freezing point.	Collected at	Freezing point.	Collected at	Freezing point.
1	133°	56·0°	133—134°	56·3°	134—135°	56·1°
2	134	56·0	134	56·2	134—135	56·2
3	133—134	56·1	134	56·0	134—136	56·3

These results indicate that the β-form distils unchanged at 133—136°/20 mm. The distillate was a pale yellow, mobile liquid, which readily solidified in the receiver. The freezing-point determinations show that there is no appreciable difference in composition between the separate fractions.

Mixed Crystals of Intermediate Composition.—The reaction product was used for these experiments. It was purified by a single crystallisation from neutral aqueous alcohol. The following result is typical of many that were obtained with crystals of different freezing points:

Freezing point of substance used.	Fraction.	Collected at	Character.	Approx. quantity.	Freezing point of fraction.
80°	A	134—135°	Mobile, colourless, froze in receiver	5 c.c.	70°
	B	135—235°	As A at first, then as C	5 ,,	75
	C	235—237°	Viscid, deep yellow, solidified with difficulty	5 ,,	96—97

These experiments show that it is, to a certain extent, possible to separate a mixture of the isomerides by this method. The temperature remains between 130° and 140°, whilst products distil over, the freezing points of which range from 56° to 70°. In the case of the mixtures of higher freezing point, such as the above, the temperature then rises quickly through 100°, during which time very little passes over. At 235° the boiling again becomes vigorous, but the character of the distillate is very different, and the freezing point indicates that it consists mainly of the α-form.

α-Form.

The following is a typical result:

Freezing point of substance used.	Fraction.	Collected at	Character.	Approx. quantity.	Freezing point of fraction.
98°	A	135—236°	Thin at first, then viscid	2—3 c.c.	92°
	B	236—237	Viscid and yellow	12 ,,	98—99

The behaviour is qualitatively the same as that of the reaction product. The rapid rise occurs earlier in the experiment, and the main portion consists of the higher boiling fraction.

Discussion of Results.

The chief result of this work has been to confirm in more detail many of Lockemann and Liesche's statements. The freezing-point curve definitely proves that the two forms are isomorphous, and form a continuous series of mixed crystals. They have, moreover, the same density, and undergo no physical change—even in optical properties—when transformation takes place.

Lockemann and Liesche state that the β-form rises in melting point when stored in a neutral medium, and draw the conclusion that the α-variety is the stable form. This observation could not be confirmed. Alone, whether in the solid, liquid, or gaseous state, when oxidation is prevented, each isomeride seems perfectly stable: the α- and β-forms, and all intermediate mixtures of them, undergo no change whatever, but, excepting (probably) when moisture is rigidly excluded, the presence of acid causes transformation to the lower melting end of the series of mixed crystals, whilst the presence of alkali causes the opposite transformation.

The peculiarity of the isomerism is obviously connected with the very small difference in energy content, and therefore in the relative stability of the two forms. On the other hand, there can be no doubt that the α-form is more stable in presence of alkali and the β- in presence of acid, and that a trace of acid or alkali can bring about a change from one to the other, proceeding through a mass of crystals without their passing into solution. It therefore follows that there is a difference between the crystals in contact with acid and crystals in contact with alkali. This can only come about by adsorption of acid or alkali into the crystals, which causes a difference in energy greater than the difference between the two absolutely pure forms.

No trace of acid or alkali could be found in the crystals by direct experiment, but this is not a very serious objection. The total

quantity of acid or alkali present is very small indeed, and the partition-coefficient would doubtless be greatly in favour of the water, of which there is a much larger quantity present, that is, the amount of acid or alkali in the crystals would be excessively small.

The influence of a solvent is clearly to give an equilibrium mixture. In the general case of two isomerides forming a solid solution, the stable form is, of course, one particular solid solution of a composition independent of the liquid present. The results show that the freezing point of the equilibrium mixture obtained from various solvents is as follows:

Solvent.	Freezing point of equilibrium mixture.
Light petroleum	82·5
Ether	82·8
Water	81·0
Alcohol (highest)	78·0

The results in alcohol are untrustworthy for reasons explained above. The differences observed may be due to experimental error —traces of acid, etc.—or they may be due to adsorption of the solvent producing a similar, although smaller, effect to that of acid or alkali. The composition indicated by a freezing point of 82·5° is 75 per cent. of *α* and 25 per cent. of *β*. In this connexion it is interesting to note that Fischer described three forms of the substance in question. His third variety, melting about 80°, corresponds with this equilibrium mixture.

It seems probable that the isomerism is stereochemical. Lockemann and Liesche have pointed out that isomerism is very common in hydrazones of the type $\begin{array}{c}A-C-B\\ \|\\ N\cdot NH\cdot C_6H_5\end{array}$, but not in those of the type $\begin{array}{c}A-C-A\\ \|\\ N\cdot NH\cdot C_6H_5\end{array}$, where stereoisomerism is excluded. The structural isomeride, benzeneazoethane, $CH_3\cdot CH_2\cdot N\colon N\cdot C_6H_5$, has been prepared by E. Fischer, and is a red oil.

Several closely allied compounds were investigated in the same way. Acetaldehyde-*p*-bromo- and -*p*-nitro-phenylhydrazones were not found to exhibit isomerism when tested by the above methods, but a similar, although less defined, behaviour was found in the case of acetaldehyde-*p*-tolylhydrazone.

DAUBENY LABORATORY,
MAGDALEN COLLEGE, OXFORD.

CCXXXVIII.—*Theory of Dyeing: the Colour and Molecular State of Picric Acid.*

By William Porter Dreaper, F.I.C.

Picric acid in the anhydrous state is probably colourless. It is nearly so under conditions of long exposure to the action of dehydrating agents acting through a vacuum.

In the colourless condition it has been regarded as having an *o*- or *p*-quinonoid constitution.

An investigation into variations in the conditions of formation of the colourless variety in the presence of fibre colloids (Dreaper and Stokes, *J. Soc. Dyers*, 1909, **25**, 10) with the results now recorded has led to this consideration of the possible molecular structure in relation to its behaviour under these conditions. It may be mentioned that Vignon (*Rev. Gen. Mat. Col.*, 1909, 13, 156) has compared the dyeing properties of picric acid with the electrical conductivity of its solutions, and that Dreaper and Davis (*Internat. Congr. Appl. Chem.*, 1909, Sect. IV*b*, 7) have confirmed that picric acid in aqueous solution is not subject to de-solution when passing through a sand column. Walker and Appleyard (Trans., 1896, **69**, 1334) have also discussed the dyeing action of picric acid on silk, and have shown that the law of the distribution of picric acid at 60° is:

$$s/\sqrt[2\cdot7]{w} = 35\cdot5.$$

It has been assumed for the purpose in hand that the condition of attraction or strain exhibited by atoms for one another, and the attraction observed as between molecule and molecule, is identical, and in both cases can be referred back to the attraction of atoms acting at varying distances; thus, molecular attraction is regarded as primarily due to the attraction of the atoms in one molecule for those in the surrounding molecules within the active sphere of influence, and not to the attraction of molecule for molecule (see *Chem. News*, 1905, **92**, 299; *Proc. Faraday Soc.*, 1910, 31). It is further assumed that the sum of the primary attraction (as between atom and atom in the same molecule) and the secondary attraction (as between an atom in one molecule and those in others) is at its maximum a constant. The secondary attraction under these conditions would increase as the primary attraction decreases.

It is assumed for the moment that the picric acid molecule is actually in association with *x* molecules of water (dihydrone or hydronol) in the coloured type. It is difficult to escape this conclu-

ion if this is the cause of a change in molecular structure, and the ollowing facts must then be considered.

The colour intensity apparently increases to a maximum before ctual solution takes place, and the ratio of the assembled molecules f water to those of picric acid has increased to a degree where uch a change in physical state is involved. Change of colour is herefore not connected in this case with actual solution, unless it s assumed that the one type of picric acid is in solution in the ther.

Assuming, therefore, that an association of the order suggested xists, and that this is as between atom and atom, although appa- ently expressed by outward molecular attraction, and, further, hat this attraction under certain conditions may be localised, it vill then involve either the H·, NO_2·, OH·, or O groups. Any econdary association may then be represented as follows:

$$-H..OH_2,\ -NO_2..OH_2\cdot,\ -OH..OH_2\cdot,\ \text{or}\ -O..OH_2\cdot,$$

It will be observed that the last combination is the only one nown to exist in the free state. It is suggested that this possible ddition correspondingly induces secondary attraction of a localised der, which may then take place as between such units. The sumption that the sum of the primary and secondary attractions is a maximum value has in this respect a definite significance. he effect of such localisation will be to reduce the general attrac- on (as between molecule and molecule), the former taking its lace. If ordinary attraction as between atom and atom be repre- nted by . localised attraction may be written as . . and general ttraction as influencing molecule and molecule as . . .

It is seen that association of this localised order is only possible ith the quinone or an equivalent type. An equilibrium condition etween the picric acid and water molecules may be set up, under hich there is a tendency for the colourless type to be replaced y the coloured one.

It is then assumed that the secondary attraction as between the $(OH_2)_x$ molecules and the oxygen atom is sufficient to displace the quilibrium existing between the two types in the direction indi- ated, and to suppress the ordinary type in favour of the coloured ne. The above attraction between the $(OH_2)_x$ molecules and the xygen atom would under these conditions partly replace that of he ·H atom, and the latter would under these conditions of strain igrate to the neighbouring NO_2-group, with the formation of a ompound of quinonoid type.

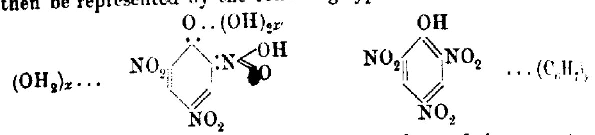
If this localised affinity exists, the oxygen atom, from its isolated osition and the fact that it is in combination with a monatomic ydrogen atom, might favour such an action. Be this as it may,

the above consideration affords a possible explanation of the cause of the action observed if the quinone type is actually formed, and if this action is accepted as the cause of the colour change.

The solvent action of toluene when it replaces water is of a different order. In this case the colourless type is present to the virtual exclusion of the coloured one. The yellow variety dissolves to a colourless solution. It must be assumed in this case that association is of a more general order, and non-localised. There is no side-group which can associate with the solvent molecules in the manner suggested in the case of water.

By mass action the water associated with the picric acid in solution is replaced by toluene, and the colourless type is once more in stable equilibrium with the solvent.

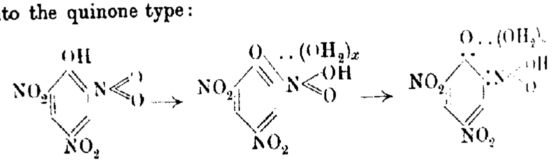
Solutions of picric acid in water and toluene respectively may then be represented by the following types:



In the former case water is represented as being associated locally (. .) as well as generally (. . .). The secondary association may naturally be modified by certain internal groupings, possible close-packing of the atoms, etc., with their attendant condition of strain.

It must be considered whether there is not a more convenient method of considering the change which takes place from one type to the other. If the hydrogen atom migrates, it may well carry with it its bond of attraction, and the change may then be indicated in the following manner. As the mechanism of change in intramolecular condition is apparently in this case a simple one, the change may not necessarily entail the production of the quinone type to allow of salt formation, etc.

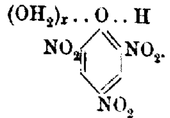
The colour may have its origin in a change of type as indicated below in the intermediate type, which, if unstable, may then pass into the quinone type:



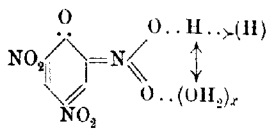
x may or may not equal y in this case.

Alternate methods of association may suggest themselves for comparison with the above. In the quinone type, association may be as between the side-groups generally and the water molecules.

wing to position, but this does not seem to be the case in a solution n toluene; or association may take place as between the $(OH_2)_x$ . . roup and the other oxygen atom, as follows:

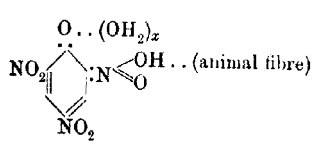


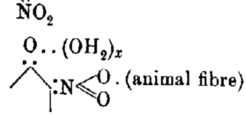
It will be remembered that the loss of colour has also been scribed to the suppression of free hydrogen ions. In that case of ssociation the presence of free or migrating ions is not impossible, owing to the reduction in the primary bond and an interchange of atoms from one molecule to the other under this condition. This action might be represented graphically in the following manner:

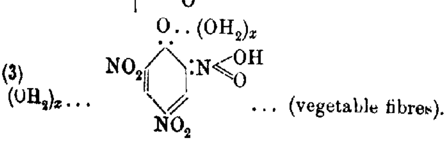


Association may therefore be of a general order, except where onditions are present which supply a tendency to form separate roups or independent units, and then association may be localised n the manner suggested. In the latter case the modification in he general state of equilibrium may be sufficient to disturb the eneral system and induce certain changes, as in the case of water nd picric acid.

The salts of picric acid are coloured, and may be regarded as eing of the quinone type. The association as between picric acid nd animal and vegetable fibre respectively, where in the former ase the change from the coloured type to the colourless does not ake place in a vacuum, may possibly be expressed in the following erms:

(1) 

r even (2) 

nd (3) 

The colour change can take place in (3), but not in (2), and in the case of silk dyed at 15°, where a certain loss of colour is observed in a vacuum, the change observed may take place in (1), which may be present at such low temperatures of dyeing. This agrees with the experimental results.

Experimental.

The rate of change from the coloured to the colourless type of picric acid when present on the fibres under the action of certain dehydrating agents acting in a vacuum has thus been shown to be of a definite order (Dreaper and Stokes). On vegetable fibres the change is facilitated, whilst on animal fibres it is entirely prevented.

The comparative action of water and toluene on picric acid present within the fibre area has now been examined, it being known that picric acid dissolves in toluene, giving an almost colourless solution.

Silk (fibroïn) was dyed at 95° in the usual manner from an aqueous solution containing 3 per cent. of picric acid of the weight of silk taken, the ratio of silk to solution being 1:200. On immersion in toluene no change in colour or any appreciable re-solution of the dyestuff in the solvent could be observed. This result agrees with that previously obtained with the silk fibre substance and picric acid in a vacuum where this inter-relation prevents any change in type taking place under conditions on which picric acid itself loses colour. As the yellow variety of picric acid passes immediately into a colourless state on solution in toluene, the union between the picric acid and silk fibre-substance evidently prevents the normal change to the colourless type.

When cotton replaces silk, the results are of a different order from those obtained with dehydrating agents. When this fibre is coloured or stained with picric acid from a saturated aqueous solution of the latter, the picric acid is held so loosely that resolution in water is immediate, the colour being removed on agitation with water (ratio of fibre to water = 1:1000) in twenty seconds. On the other hand, practically no loss occurred from the fibre area after thirty minutes' extraction with toluene at 17°, nor could any material change from the coloured to the colourless type be observed. The yellow variety is therefore stable (and insoluble) under the conditions indicated.

Following this result, it was observed that cotton may under certain conditions absorb picric acid and dye the fibre an intense yellow shade from its colourless toluene solution. This action seems to depend on the presence of oxycellulose. Under these conditions silk remains colourless, so that the dyeing properties of picric acid

in toluene as judged by colour indications are the reverse of those exhibited in aqueous solution, where the yellow variety is present within the silk area, and the cotton, except in a solution of high concentration, remains white, and absorbs no picric acid.

The silk remained colourless on evaporating the toluene, and the cotton still exhibited a full and brilliant shade of yellow. Samples treated in this manner were subjected to the action of water vapour at 100° and 15° respectively. The silk gradually assumed a yellow shade, and the cotton also visibly deepened in shade; but in water under the conditions before mentioned, the cotton still lost all its colour in twenty seconds; the silk lost about 60 per cent.

A development in shade was noticed on exposure to a damp atmosphere in the place of steam, but the rate of change from the colourless to the coloured type within the fibre area was not so rapid or so complete as after the action of the dehydrating agents, as previously recorded.

The influence of the presence of moisture in the cotton on the result obtained was next investigated. A sample was dried at 110° for one hour, and another was treated with steam before immersion in a solution of picric acid in toluene. The dried sample was much lighter in shade, and the steamed one darker. Taking the depth of shade of the ordinary cotton after treatment as 100, the dried one was represented by 70 and the steamed one by 150. After forty-eight hours' exposure of the samples so treated to the action of a saturated atmosphere at 15°, all the samples developed in colour to a standard shade, indicating that the depth of colour assumed by the fibre at the time of contact is no guide to the amount of picric acid actually absorbed, but only of the proportion of the moisture present in the cotton fibre area.

Cotton containing 6—8 per cent. of natural moisture developed a yellow shade under these conditions, whilst silk containing 10—12 per cent. of natural moisture remained colourless. The nature of the condition under which the water is present within the cotton and silk fibre area is therefore a determining factor. It is possible that in the case of silk the toluene may not penetrate into the silk substance, and therefore no absorption of picric acid can take place; but this does not agree with some of the results obtained. It may be noted that the former assumption has been held to explain certain obscure reactions which occur in the practical manipulation of these fibres.

A sample of silk was immersed in water, and all superfluous moisture carefully removed under pressure in a dry cloth. On subsequent immersion in the toluene solution the silk at once assumed a fairly deep shade of yellow, indicating that the yellow

variety can exist under these conditions in the silk fibre. The action was a non-reversible one, for after drying to remove interfering moisture the colour remained to its full intensity on subsequent immersion in toluene. When once the conditions in the animal fibre are present which determine the formation of the yellow variety, it is apparently more stable than the colourless one.

Sisley has noticed that in dilute solution the whole of the picric acid is present in the water in a mixture of water and toluene, and even in strong solution the ratio is still 4 : 1. The subsequent development of colour in the above samples containing varying amounts of moisture to a common shade does not indicate that the actual adsorption is directly caused by the presence of moisture. This condition seems to govern the ratio of change from the colourless type to the coloured one.

In the case of silk the natural resistance against change is probably due to the fact that the moisture present is in some closer relationship with the fibre colloid, and that this prevents it from reacting with, and producing the colour change with, picric acid observed in the case of cotton; but this change can take place in the presence of water, which is not so closely associated with the fibroin. When the change has taken place as in the case of a silk fibre which obviously contained "free" moisture, some further action between the silk substance and the yellow type prevents the subsequent reversion to the colourless type in the presence of toluene.

Thus, whilst "free" moisture must be present in order that the yellow variety may exist in the silk fibre area, yet there is an adsorption of the colourless variety from toluene in its absence. This follows from the fact that on subsequent steaming the colourless silk develops a yellow shade, even after a final treatment with toluene to remove any surface picric acid which in itself might account for this action.

The relationship which exists between an animal fibre-substance and picric acid which prevents or inhibits the loss of colour on exposure to the dehydrating agents, and resists resolution and a return to the colourless type in the presence of toluene, is apparently different in the case of vegetable fibres. The action of dehydrating agents in this case causes the cotton to lose its colour, but does not do this in the presence of toluene, so that these reactions indicate in further detail the nature of the affinity which apparently exists between the fibre and the picric acid.

It may be argued that an affinity exists between the picric acid and cotton fibre-substance which prevents the normal change to the colourless type taking place in the presence of toluene; so that

whilst the picric acid is easily removed by water from the fibre area, this action cannot take place in the case of toluene. This agrees with the assumption that the yellow variety is insoluble as such in toluene, and that the latter cannot bring about a change of type in the presence of the cotton fibre-substance. The yellow variety being soluble in water is easily removed. As picric acid will dye cotton from a toluene solution, it may be argued that this suppression of colour change is not due to any want of penetration of the solvent into the fibre.

The results obtained may be summarised in the following manner:

Nature of Fibre.	Action of dehydrating agents acting through a vacuum.	Action of toluene on picric acid within the fibre area.
Silk	No loss in colour	No loss in colour
Wool	,, ,,	,, ,,
Cotton	Loss of colour in excess of that in acid itself	,, ,,

CCXXXIX.—*Formation of Six- and Seven-membered Rings from Derivatives of 2 : 2'-Ditolyl.*

By JAMES KENNER and EMILY GERTRUDE TURNER.

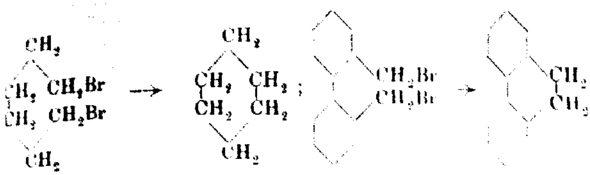
THE general problem of the formation of closed rings from open-chain compounds has been the subject of repeated investigation, and in their broad outlines the results may be said to be capable of interpretation in terms of Baeyer's strain theory. Whilst, however, the stability, and therefore presumably the readiness of formation, of any ring is largely determined by the number of carbon atoms composing it, the relative position and nature of the substituent groups also play an important part. Although comparatively little attention has been bestowed on this side of the subject, it is possible to say: "dass im allgemeinen das Vorkommen eines quaternär gebundenen Kohlenstoffatoms die Aufspaltbarkeit zu erhöhen scheint" (Aschan, "Chemie der alicyclischen Verbindungen," 1905, p. 244), and, further, that the rupture of the ring takes place at the point where this atom occurs. It seems not impossible that the various groups attached to the carbon atom have an effect on each other similar in nature to that which is assumed to give

rise to the phenomena of steric hindrance and inhibition, or in other words, that a more extended application of Baeyer's theory is required. From this point of view it is to be expected that the ease with which cyclic condensation occurs will be modified by the presence in the chain of some carbon atoms which, being already members of a closed ring, have the directions of their valencies to some extent determined. The extent of this modification, should it occur, will necessarily be determined by the number of the carbon atoms of this type involved in the production of the new ring and by the degree of strain to which those of their valencies already engaged were subjected.

At the present time the compounds most easily obtainable for the study of this type of cyclic condensation are those in which certain of the carbon atoms form part of six-membered rings; thus *o*-xylene and its derivatives, the *peri*-derivatives of naphthalene and 2:2′-derivatives of diphenyl respectively contain two, three, and four such atoms. The possibility of forming rings from xylene and naphthalene has been investigated frequently, but as a result of the difficulty which formerly doubtless attended their preparation, diphenyl derivatives have received little attention. Ullmann's discovery that 2:2′-ditolyl is readily obtained by the action of copper powder on *o*-iodotoluene (*Annalen*, 1904, **332**, 28) has removed the difficulty in this case, and, as the method proved to be suitable for the preparation of the compound in quantity, we were encouraged to undertake a systematic investigation of the formation of closed rings from it.

In the first place, ωω′-dibromo- and ωωω′ω′-tetrabromo-2:2′-ditolyl were prepared. It was found that 2:2′-ditolyl reacted vigorously with bromine at 110°, and the dibromo-derivative was readily isolated. The further bromination was considerably more difficult, and only those preparations of the tetrabromo-derivative were successful in which the addition of the bromine extended over a period of at least two days.

The action of sodium on polymethylene dibromides is well known as a fruitful method for the synthesis of closed-ring compounds, and was shown by Haworth and Perkin (Trans., 1894, **64**, 599) to give excellent results when applied to hexamethylene dibromide, of which ωω′-dibromo-2:2′-ditolyl is a derivative. In the case of the latter substance, it was found that its ethereal solution readily reacted with sodium when the mixture was heated. The reaction to some extent followed a course similar to that observed for hexamethylene dibromide:



for the presence of dihydrophenanthrene in the product was readily shown by its oxidation to phenanthraquinone. The yield of phenanthrene derivative was not as favourable as that of *cyclo*hexane, for there was also produced a colourless hydrocarbon, evidently of high molecular weight, the nature of which has not yet been determined.

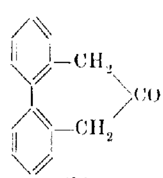
Apart from the formation of the six-membered ring in this case, this reaction has the further interest that ωω′-dibromo-2:2′-ditolyl is a possible intermediate product * in the production of dihydrophenanthrene from *o*-bromobenzyl bromide, described by Jackson and White (*Amer. Chem. J.*, 1881, **2**, 383).

By the action of sodium on ωωω′ω′-tetrabromo-2:2′-ditolyl, phenanthrene itself was obtained in good yield:

$$\begin{matrix} C_6H_4\cdot CHBr_2 \\ | \\ C_6H_4\cdot CHBr_2 \end{matrix} + 4Na \longrightarrow \begin{matrix} C_6H_4\cdot CH \\ | \quad\; \| \\ C_6H_4\cdot CH \end{matrix} + 4NaBr.$$

It may be remarked that this synthesis of phenanthrene is the first in which the hydrocarbon has been obtained by a series of reactions, all of which may be carried out at comparatively low temperatures.

Attention was then directed to the isolation of compounds containing the hitherto unknown combination of a seven-membered ring with two six-membered rings. For this purpose the preparation of the ketone (I) was attempted, as the researches of Baeyer and others have shown that such cyclic ketones constitute one of the most convenient starting points for synthetical operations of this kind:



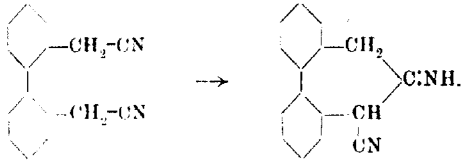
(I.)

Whilst the method involving the dry distillation of the salts of

* Experiments are in progress having for their object the preparation of another possible intermediate product, 2:2′-dibromodibenzyl, in order that the behaviour of this compound may be studied.

dibasic acids is perhaps the most generally applicable in such cases, it necessitates the use of considerable quantities of material. Moreover, the isolation of the heptanone derivative from the distillate might probably be difficult without some knowledge of its properties. This information we have sought to gain by attempting the production of the compound by other means before proceeding to investigate the conditions most suitable for its formation from 2:2′-ditolyl-ωω′-dicarboxylic acid.

2:2′-Ditolyl-ωω′-dicarboxylonitrile had been chosen as a source of this acid, and was prepared from ωω′-dibromo-2:2′-ditolyl in the manner described for *o*-phenylenediacetonitrile by **Moore** and Thorpe (Trans., 1908, **93**, 165). It was then found that this compound could be made to undergo condensation by the method applied to *o*-phenylenediacetonitrile by these authors, and we turned our attention to this condensation as likely to provide an easier means of preparing the ketone than that originally contemplated. The condensation, effected under the influence of sodium ethoxide, leads to the production of *1-imino-2-cyano-3:5-dibenzo-$\Delta^{3:5}$-cyclo-heptadiene* * (II):

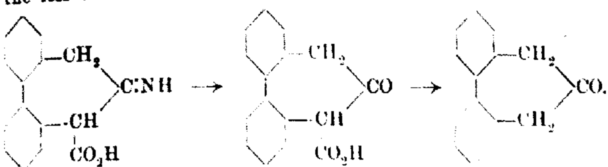


(II.)

This iminocyano-compound shows considerable stability, and is only very slowly decomposed by hot aqueous potassium hydroxide. Its behaviour towards cold concentrated sulphuric acid corresponds with that of β-imino-α-cyanohydrindene, and leads to the formation

* The system of nomenclature proposed for these compounds is based on that which has been adopted in the case of compounds in which one benzene ring is combined with a seven-membered ring. The only compounds of this type described in the Transactions (Kipping and Hunter, Trans., 1901, **79**, 602) are termed phenocycloheptane derivatives. The prefix "pheno-" seems, however, to have been generally discarded in favour of "benzo-" (compare Thiele and Schneider, *Annalen*, 1909, **369**, 288; Thiele and Weitz, *ibid.*, 1910, **377**, 1; papers by Scholl, in the *Berichte*, on benzanthrone derivatives, and Aschan, "Chemie der alicyclischen Verbindungen," 1905, p. 886). Further, as the proposed generic name emphasises the derivation of these compounds from *cyclo*heptane, any system of numbering should commence from an atom of the seven-membered ring. The choice of the particular atom is conveniently regulated by the ordinary rules of the Geneva nomenclature. The position of the "benzo-" nuclei in the heptamethylene ring is denoted according to the same plan as that in general use for double linkings. In the case of compounds containing substituents in the six-membered rings, the numbering could be continued in these rings, commencing with the carbon atom adjacent to that one

of *1-imino-3:5-dibenzo-$\Delta^{3:5}$-cycloheptadiene-2-carboxylic acid* (III). By the action of hot dilute sulphuric acid on this compound, the desired ketone, 3:5-*dibenzo-$\Delta^{3:5}$-cycloheptadien-1-one*, was obtained. This reaction can be explained by assuming that the imino-compound is hydrolysed in the first place to the corresponding keto-compound, and this, as an a-ketonic acid, is decomposed by the dilute acid, with the loss of carbon dioxide:

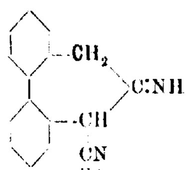


(III.)

These imino-compounds were not examined more closely than was necessary for the immediate purpose in view, but it was observed that they do not show the colour reactions with oxidising agents which are characteristic of the hydrindene derivatives described by Moore and Thorpe. These authors showed that the colour in the case of β-imino-α-cyanohydrindene is due to the formation of bis-1-cyano-2-hydroxyindene (IV):

$$CN\cdot C{<}{\scriptstyle C(OH) \atop \scriptstyle C_6H_4}{>}C{:}C{<}{\scriptstyle C(OH) \atop \scriptstyle C_6H_4}{>}C\cdot CN$$

(IV.)



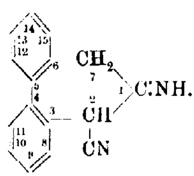
(V.)

It is not improbable that the failure of the reaction in the case of 1-imino-2-cyano-3:5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene (V) is due to steric causes, as it is unlikely that the carbon atom C can come within the sphere of action of a similar carbon atom in a second molecule of the compound.

The readiness with which phenanthrene was formed from

of the four common to two rings which takes precedence in the numbering of the *cyclo*heptane ring.

This system of numbering is shown in the diagram for the imino-compound referred to above:



ωωω'ω'-tetrabromo-2:2'-ditolyl made the study of condensations with the corresponding dialdehyde a matter of interest. This dialdehydodiphenyl * was readily obtained from ωωω'ω'-tetrabromo-2:2'-ditolyl by hydrolysis with potassium oxalate in dilute alcoholic solution. When submitted to the action of concentrated potassium hydroxide solution, on the lines of the Cannizzaro reaction, a hydroxy-acid (with its lactone) was obtained. The acid proved to be *ω-hydroxy-2-methyldiphenyl-2'-carboxylic acid*, and the analogy between this reaction and that which occurs with benzaldehyde is shown by the formulæ:

$$\begin{matrix} C_6H_5\cdot CHO \\ C_6H_5\cdot CHO \end{matrix} \rightarrow \begin{matrix} C_6H_5\cdot CH_2\cdot OH \\ + \\ C_6H_5\cdot CO_2H \end{matrix};$$

$$\begin{matrix} C_6H_4\cdot CHO \\ | \\ C_6H_4\cdot CHO \end{matrix} \rightarrow \begin{matrix} C_6H_4\cdot CH_2\cdot OH \\ | \\ C_6H_4\cdot CO_2H \end{matrix}.$$

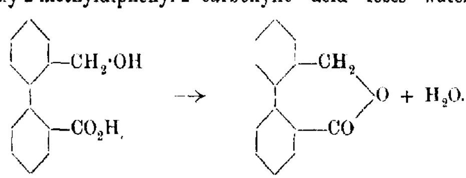
The reaction is of great interest in view of the experimental evidence adduced by Claisen (*Ber.*, 1887, **20**, 646) and by Kohn and Trantom (Trans., 1899, **75**, 1155) in support of the hypothesis that a compound (A) is formed as an intermediate product from benzaldehyde:

$$\begin{matrix} C_6H_5\cdot C(OH)(OK) \\ C_6H_5 \text{———} CH_2 \end{matrix} \!\!>\! O \qquad\qquad \begin{matrix} C_6H_4\cdot C(OH)(OK) \\ | \\ C_6H_4 \text{———} CH_2 \end{matrix} \!\!>\! O$$

A. B.

The application of this conception to the condensation of 2:2'-dialdehydodiphenyl would involve either the formation of the substance (B) or a series of similar reactions in which two separate molecules condense, as illustrated by the reaction encountered in the case of terephthalaldehyde, which leads to the formation of ωω'-dihydroxy-*p*-xylene, terephthalic acid, and ω-hydroxy-*p*-toluic acid (Grimaux, "Jahresbericht über die Fortschritte der Chemie," 1876, 490).

Actually it would seem that (B) is the intermediate product, for ω-hydroxy-2-methyldiphenyl-2'-carboxylic acid loses water when



* Since this paper was written, F. Meyer has published (*Ber.*, 1911, **44**, 2505) an account of the preparation of this compound from *o*-iodobenzaldehyde. The aldehyde was not obtained by him in the solid condition, but was characterised by the preparations of certain derivatives. The compound was first described by us (Proc., 1911, **27**, 92).

heated to 110°, forming an ε-lactone, which stands in close relationship to (B). By hydrolysis this lactone is reconverted into the hydroxy-acid.

The formation of an ε-lactone is so unusual that it is of interest to note that, so far as we are aware, only one other case has been recorded in which an ε-lactone is formed directly from the hydroxy-acid by loss of water. Baeyer and Seuffert (*Ber.*, 1899, **32**, 3619) found that βζ-dimethyloctan-ε-oloic acid readily forms a lactone, whilst Baeyer and Villiger prepared this and another ε-lactone, and even a ζ-lactone, by the action of Caro's acid on menthone, tetrahydrocarvone, and suberone respectively.

The behaviour of 2:2′-dialdehydodiphenyl just described also agrees with that of the *o*-xylene derivative, for Thiele and Günther (*Annalen*, 1906, **347**, 107) mention that *o*-phthalaldehyde yields phthalide by interaction with potassium hydroxide. Further, it is well known that diphenic acid, like phthalic acid, readily yields an anhydride on dehydration with acetyl chloride, whereas adipic acid, of which diphenic acid is a substitution derivative, under the same conditions only furnishes a small amount of anhydride, even after prolonged treatment (Étaix, *Ann. Chim. Phys.*, 1896, [vii], **19**, 356); also an imide of diphenic acid, but not of adipic acid, is known. The unusual ease with which seven-membered rings are formed in these cases supports the view that the 2:2′-position in diphenyl derivatives is frequently an effective ortho-position.* In this connexion Täuber's observation that 2:2′-diaminodiphenyl condenses with benzil in the same manner as *o*-diamines (*Ber.*, 1892, **25**, 3287; 1893, **26**, 1703) is not without interest.

If it be assumed that two double bonds are present in the 3:4- and 5:6-positions rather than in the 3:8- and 5:15-positions of the dibenzo*cyclo*heptadiene molecule, and that these double bonds have the usual stability associated with their presence in benzene rings, it may be pointed out that the strain, in Baeyer's sense of the word, is not nearly so large as is usually attributed to the *cyclo*heptane ring; for the angle between any single bond and the plane of two others is 125°16′. The *cyclo*heptadiene ring involved in the present case contains four such angles, together with three of 109°28′, amounting in all to 829°18′. The deficiency or total strain is therefore 70°32′, as contrasted with 133°44′ in the case of the saturated ring, and the average deviation of each of the fourteen valencies (the two valencies of each double bond being considered

* Experiments are contemplated with the object of determining to what extent this resemblance holds, for it may be expected that limitations will exist just as they are known to occur in the case of the relationship between the *peri*-position of naphthalene and the ortho-position.

to act together in such a case) becomes 5°2′, or rather less than the mean deviation in the *cyclo*hexane ring. A similar calculation in the case of benzene itself reveals an average strain of 2°38′. In general, the presence of such double bonds would tend to diminish the strain of rings containing six or more carbon atoms, and to increase it in the case of rings containing less than six carbon atoms.

The benzoin reaction was also applied to 2:2′-dialdehydodiphenyl in the hope that intramolecular condensation might also take place in this case, leading to the formation of 9:10-dihydroxyphenanthrene:

$$\begin{array}{l}C_6H_4\cdot CHO\\ |\\ C_6H_4\cdot CHO\end{array} \longrightarrow \begin{array}{l}C_6H_4\cdot CH\cdot OH\\ |\qquad\quad |\\ C_6H_4\cdot CO\end{array} \rightleftarrows \begin{array}{l}C_6H_4\cdot C\cdot OH\\ |\qquad\quad \|\\ C_6H_4\cdot C\cdot OH\end{array}.$$

Actually, however, it would seem that two separate molecules of dialdehydodiphenyl are concerned, for, although the amorphous product of the reaction was too ill-defined to allow of its isolation in the pure condition, it showed the reactions of a benzoin. It had reducing properties, and on oxidation was converted into an *o*-diketone, which, however, was not phenanthraquinone.

EXPERIMENTAL.

The 2:2′-ditolyl used in the following experiments was prepared according to the method described by Ullmann (*loc. cit.*) by heating equal weights of *o*-iodotoluene and copper bronze ("Naturkupfer C") under pressure at 230°. At higher temperatures the yields were not quite so good, but in all cases products of much higher boiling point accompanied the 2:2′-ditolyl.

ωω′-Dibromo-2:2′-ditolyl.

The bromination was carried out in a reflux apparatus so arranged that the bromine was introduced below the surface of the ditolyl. There was a distinct evolution of gas at 90°, but the mixture was heated at 110° in order to accelerate the reaction, which, it may be mentioned, took place more rapidly in sunlight than in the dark. After the calculated quantity of bromine had been added, the heating was continued until the evolution of gas had ceased and the dark red liquid was transparent, the temperature being raised if necessary to 120°. Neglect of this precaution in one case caused a considerable diminution in the yield. The product was kept in a vacuum desiccator over potassium hydroxide for some days while the dibromo-compound crystallised out. After adhering oil * had been separated as completely as possible, the solid was

* An attempt to utilise this oil for the preparation of the tetrabromo-derivative (p. 2112) was unsuccessful.

crystallised from acetone, being obtained in large, rhombic prisms, melting at 87·5°. The weight of pure product thus obtained amounted to two-thirds of the weight of ditolyl used:

0·1379 gave 0·2507 CO_2 and 0·0442 H_2O. C=49·57; H=3·56.

0·1868 „ 0·2083 AgBr. Br=47·44.

$C_{14}H_{12}Br_2$ requires C=49·41; H=3·56; Br=47·02 per cent.

Action of Sodium on ωω'-Dibromo-2:2'-ditolyl.

The dibromo-derivative dissolved in dry ether was gently boiled with successive quantities of sodium powder until the metal was no longer attacked. After decantation and removal of the ether, a mobile oil was obtained, from which after some days a minute quantity of unchanged dibromide separated. Beyond this, no separation could be obtained, an unexpected result, as dihydrophenanthrene melts at 94—95° (Schmidt and Mezger, *Ber.*, 1907, **40**, 4248). To discover if this substance had been produced, a portion of the oil was treated with picric acid solution in the manner described by these authors, and the characteristic colour change from yellow to red was observed, although attempts to separate the red picrate from the excess of picric acid were unsuccessful. Eventually the yield of dihydrophenanthrene was estimated by oxidising the oil with a solution of chromic acid in glacial acetic acid, and found to be 26 per cent. The phenanthraquinone after purification melted at 205°, answered all the well known reactions, and, further, was identified by analysis. (Found, C=80·56; H=3·99. Calc., C=80·76; H=3·88 per cent.)

During the action of sodium on the ethereal solution just described, the separation of a colourless, amorphous substance was observed. This was soluble in benzene, but resisted all attempts to crystallise it, being obtained as a brittle deposit after evaporation of the solvent, and has not been examined further than to show that it is free from halogen.

2:2'-Ditolyl-ωω'-dicarboxylonitrile.

The methods used in the preparation of this compound and of its derivatives were essentially those applied by Moore and Thorpe (*loc. cit.*) in the case of *o*-phenylenediacetonitrile.

A saturated aqueous solution of potassium cyanide (5·2 grams) was mixed with about three times its volume of absolute alcohol. The mixture was heated to the boiling point, and to it finely powdered ωω'-dibromo-2:2'-ditolyl (12 grams) was added in small portions. After remaining at 50—60° for some hours, water was added to the product, and the nitrile obtained as an oil which

readily solidified, and, after crystallisation from alcohol, formed rectangular blocks, melting at 77°. The yield was about 90 per cent. of the calculated amount:

0·1658 gave 17·15 c.c. N_2 at 15·5° and 747 mm. N=12·04.
$C_{16}H_{12}N_2$ requires N=12·09 per cent.

2:2′-*Ditolyl-ωω′-dicarboxyamide.*

This compound was prepared by allowing the solution of the nitrile in five times its weight of concentrated sulphuric acid to remain overnight. On pouring the mixture into water and rendering the solution alkaline with ammonia, a quantity of the amide was precipitated, the weight of which was rather less than that of the nitrile used. This compound is only sparingly soluble in benzene, chloroform, or light petroleum, but dissolves readily in alcohol, from which it separates in clusters of fine needles, melting at 210—211°:

0·1452 gave 0·3800 CO_2 and 0·0810 H_2O. C=71·37; H=6·19.
0·1280 „ 12·1 c.c. N_2 at 25° and 752 mm. N=10·67.
$C_{16}H_{16}O_2N_2$ requires C=71·64; H=5·97; N=10·45 per cent.

2:2′-*Ditolyl-ωω′-dicarboxylic Acid.*

The hydrolysis of the amide just described was effected by boiling it with 10 per cent. potassium hydroxide solution until the evolution of ammonia, which was only slow, had ceased. After acidification, the product was repeatedly extracted with ether, and, after removal of the ether, crystallised from water. 2:2′-*Ditolyl-ωω′-dicarboxylic acid* crystallises in prisms, melting at 152°:

0·1438 gave 0·3750 CO_2 and 0·0698 H_2O. C=71·17; H=5·23.
$C_{16}H_{14}O_4$ requires C=71·12; H=5·22 per cent.

1-*Imino-2-cyano-3:5-dibenzo-$\Delta^{3:5}$-cycloheptadiene.*

To prepare the imino-compound a solution of 2:2′-ditolyl-ωω′-dicarboxylonitrile in four times its weight of absolute alcohol was boiled with a small amount of sodium ethoxide for one hour in a current of hydrogen. After about half an hour the imino-compound began to separate from the hot solution in colourless, prismatic crystals, and the yield amounted to over 80 per cent. of that calculated. The product melted at 189°:

0·1179 gave 0·3562 CO_2 and 0·0586 H_2O. C=82·4; H=5·53.
0·1336 „ 0·4034 CO_2 „ 0·0634 H_2O. C=82·25; H=5·27.
0·1988 „ 20·4 c.c. N_2 at 23° and 754 mm. N=11·72.
$C_{16}H_{12}N_2$ requires C=82·76; H=5·17; N=12·07 per cent.

As this compound does not give a colour reaction with concentrated sulphuric acid or with alcoholic potassium hydroxide, it might be expected that no advantage would result from the maintenance of an oxygen-free atmosphere during the preparation, but experience showed that better results were always obtained when hydrogen was used.

Ammonia was evolved only slowly when the imino-compound was boiled with 20 per cent. potassium hydroxide solution, and the decomposition was not complete even after two days.

1-*Imino*-3:5-*dibenzo*-$\Delta^{3:5}$-cyclo*heptadiene*-2-*carboxylic Acid.*

A solution of 1-imino-2-cyano-3:5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene (4 grams) in cold sulphuric acid (40 c.c.) was left overnight, and then poured on to ice. After some time the precipitate was collected and found to be completely soluble in sodium hydroxide solution. The acid was therefore free from amide, and, after reprecipitation, was crystallised from dilute alcohol. It formed colourless needles, melting at 180°:

0·1910 gave 0·5328 CO_2 and 0·0890 H_2O. C=76·08; H=5·18.
0·2172 „ 11·0 c.c. N_2 at 29° and 759 mm. N=5·68.
$C_{16}H_{13}O_2N_2$ requires C=76·49; H=5·18; N=5·58 per cent.

3:5-*Dibenzo*-$\Delta^{3:5}$-cyclo*heptadien*-1-*one*.

A mixture of 1-imino-3:5-dibenzo-$\Delta^{3:5}$-*cyclo*heptadiene-2-carboxylic acid (3 grams) with 50 per cent. sulphuric acid (100 grams) was boiled in a reflux apparatus until all the solid had disappeared, a change which was complete after about one and a-half hours. By extraction with ether the ketone was isolated, being obtained as an oil, which completely solidified after some time. It separated from alcoholic solution in large, faintly yellow, hexagonal crystals, melting at 78—79°, but if isolated from the acid liquid by distillation with steam it is colourless. The yield was 80 per cent. of that calculated:

0·1054 gave 0·3342 CO_2 and 0·0568 H_2O. C=86·55; H=5·99.
$C_{15}H_{12}O$ requires C=86·54; H=5·77 per cent.

The *oxime* crystallises in needles from dilute alcohol, and melts at 189°. For analysis it was dried at 130°:

0·2688 gave 16·2 c.c. N_2 at 27° and 750·5 mm. N=6·58.
$C_{15}H_{13}ON$ requires N=6·27 per cent.

ωωω′ω′-Tetrabromo-2 : 2′-ditolyl.

The bromination of 2 : 2′-ditolyl was carried out in its earlier stages at 110°, the temperature being gradually raised to 140°, and about 10 per cent. more than the calculated quantity of bromine was used. Experiments in which all the bromine was added in the course of one day repeatedly failed to give more than a minute proportion of the tetrabromo-derivative, but by arranging that the addition extended over more than two days a quantity of the tetrabromo-derivative, rather less in weight than the ditolyl used, was obtained. If the bromination had been properly conducted, the dark-coloured oil immediately became very viscous when poured into a dish, but did not crystallise when kept over potassium hydroxide in a desiccator. The mass set solid when it was treated with a little warm light petroleum, and was then crystallised from this solvent. The tetrabromo-derivative resembles the dibromo-derivative in crystalline form, and melts at 138°:

0·1612 gave 0·2015 CO_2 and 0·0302 H_2O. C = 34·10; H = 2·08.
$C_{14}H_{10}Br_4$ requires C = 33·75; H = 2·02 per cent.

Action of Sodium on ωωω′ω′-Tetrabromo-2 : 2′-ditolyl.

The reaction was carried out in the same manner as in the case of the dibromo-derivative. The ethereal solution from 10 grams of the tetrabromo-derivative gave 2·4 grams of crude phenanthrene (m. p. 98°). By crystallisation from 70 per cent. alcohol, the hydrocarbon was obtained in white leaflets (Found, C = 94·15; H = 6·00. Calc., C = 94·34; H = 5·66 per cent.), from which, for purposes of identification, the picrate (yellow needles, m. p. 143°) was prepared.

2 : 2′-Dialdehydodiphenyl.

When ωωω′ω′-tetrabromo-2 : 2′-ditolyl is heated at 130° with sulphuric acid, partial carbonisation instead of the expected hydrolysis takes place, accompanied by evolution of bromine, hydrogen bromide, and sulphur dioxide, a considerable amount of the tetrabromo-derivative being recovered unchanged. Recourse was therefore had to the method of hydrolysis described by Thiele and Günther (*Annalen*, 1906, **347**, 107) for the preparation of *o*-phthalaldehyde from *o*-xylylene tetrabromide. Ten grams of ωωω′ω′-tetrabromo-2 : 2′-ditolyl were heated in a reflux apparatus on the water-bath with 20 grams of potassium oxalate and 200 c.c. of 50 per cent alcohol. The substance had dissolved completely after forty hours' boiling, and the pale yellow solution was then

added to twice its volume of water. The aldehyde separated after some hours, the yield amounting to that calculated.

The aldehyde is best purified by adding light petroleum (b. p. 40—60°) to its solution in ether, and is thus obtained in leaflets, colourless when pure, but frequently slightly yellow, and melting at 62°. It can also be crystallised from light petroleum (b. p. 60—80°), but the process of solution is accompanied by the formation of a considerable amount of oily matter:

0·0972 gave 0·2860 CO_2 and 0·0428 H_2O. C = 80·25; H = 4·89.
$C_{14}H_{10}O_2$ requires C = 79·98; H = 4·80 per cent.

The *phenylhydrazone* crystallises in rectangular prisms from alcohol, and when exposed to light changes in colour from a light yellow to a bright red:

0·1424 gave 16·2 c.c. N_2 at 26° and 756 mm. N = 13·17.
0·1528 „ 16·8 c.c. N_2 „ 26° „ 756 mm. N = 12·73.
$C_{26}H_{22}N_4,C_2H_5{\cdot}OH$ requires N = 12·88 per cent.

Action of Potassium Hydroxide on 2:2′-Dialdehydodiphenyl.

Two grams of the finely powdered aldehyde were well shaken with a cold solution of 20 grams of potassium hydroxide in 14 c.c. of water until an emulsion had been formed. After twenty-four hours the mixture was diluted and repeatedly extracted with ether in order to remove any colouring matter due to impurity in the aldehyde. The solution was then cooled and acidified. After a short time the precipitate (1·9 grams) was collected, and roughly separated into its components by treatment with ammonia solution.

The undissolved portion, purified by crystallisation from dilute alcohol, was obtained in elongated prisms, melting at 132°. From absolute alcohol it crystallised in diamond-shaped prisms:

0·1270 gave 0·3708 CO_2 and 0·0550 H_2O. C = 79·63; H = 4·81.
0·0714 „ 0·2080 CO_2 „ 0·0308 H_2O. C = 79·45; H = 4·7.
$C_{14}H_{10}O_2$ requires C = 80·00; H = 4·76 per cent.

The portion soluble in ammonia was re-precipitated by acid, and purified by repeated crystallisation from a mixture of ether and light petroleum (b. p. 40—60°), in the latter of which solvents it is sparingly soluble. It separated in small, well-defined, prismatic crystals, which melted at 146°:

0·1348 gave 0·3654 CO_2 and 0·0636 H_2O. C = 73·93; H = 5·24.
$C_{14}H_{12}O_3$ requires C = 73·68; H = 5·26 per cent.

The composition of the two substances thus pointed to the existence of a relationship between them of lactone to hydroxy-acid, and their intimate connexion was further illustrated by the conversion of the former substance into the latter through the agency

of potassium hydroxide solution, and by the observation that the acid substance lost the elements of water at 110° and passed into the non-acid product.

In conclusion, the authors desire to express their thanks to Professor Wynne for much encouragement and advice during the course of this work.

THE UNIVERSITY,
SHEFFIELD.

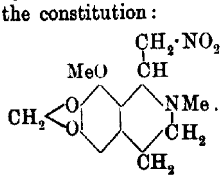
CCXL.—*Synthetical Experiments in the Group of the isoQuinoline Alkaloids. Part II. The Constitution of the Condensation Products of Cotarnine and the Condensation of Cotarnine with Aliphatic and Aromatic Nitro-compounds.*

By EDWARD HOPE and ROBERT ROBINSON.

THE peculiar reactivity of cotarnine towards nitro-compounds was first observed in the case of the condensation of this substance with nitromeconine (Hope and Robinson, Proc., 1910, **26**, 228), whereby nitrognoscopine (nitro-*r*-narcotine) resulted, and in Part I. of this investigation an account has been given of a closely related reaction, namely, that resulting in the production of anhydrocotarnine-5-nitrophthalide (this vol., p. 1153). By elimination of the nitro-group this substance was converted into anhydrocotarninephthalide, which may also be called dedimethoxygnoscopine, and the method of synthesis of alkaloids of the *iso*quinoline group which was thus indicated appeared to be worthy of a detailed examination.

The object of the present communication is to place on record the preparation of a number of compounds derived from cotarnine by condensation in the main with nitrotoluenes, and some of these, and also the condensation product with nitromethane, we propose to examine further, especially with a view to their conversion into bases free from nitro-groups allied in constitution to the naturally occurring *iso*quinoline alkaloids.

Cotarnine condenses with particular readiness with nitromethane, and the product is a crystalline base, *anhydrocotarninenitromethane*, to which we ascribe the constitution:



Although there can be no doubt that the substance is homogeneous, two distinct methiodides are obtained by the action of methyl iodide; the one produced in larger amount is probably the normal methiodide, whilst the other, a bright yellow substance, yields trimethylamine on treatment with alkali, a fact which in conjunction with analytical data indicates it as possessing the constitution:

$$CH_2{:}O_2{:}C_6H(OMe)<^{CH{:}CH\cdot NO_2}_{CH_2\cdot CH_2\cdot NMe_3I}\cdot$$

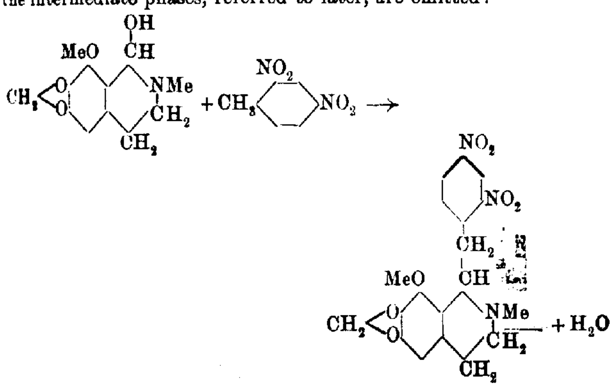
Nitroethane also yields a condensation product with cotarnine, but it has only been isolated in the form of its methiodide, whilst the other nitro-paraffins, such as the two nitropropanes and nitropentane, apparently react with great difficulty.

A series of nitrobenzylhydrocotarnines is produced by the condensation of cotarnine with nitrotoluenes.

The mononitro-compounds are obtained in moderate yield by the condensation of cotarnine with *o*- or *p*-nitrotoluene in the presence of sodium ethoxide in alcoholic solution. They are stable bases not decomposed on boiling with glacial acetic acid.

The dinitro-compounds are produced in almost quantitative yield by boiling an alcoholic solution of cotarnine and dinitrotoluene. 2:4:6-Trinitrotoluene on suspension in a cold alcoholic solution of cotarnine yields the theoretical amount of *anhydrocotarnine-2:4:6-trinitrotoluene*, the reaction being complete in a few seconds. Trinitro-*m*-xylene is less reactive, and cotarnine residues attach to both methyl groups, whilst with trinitromesitylene an even more sluggish reaction is observed, and the product is *dianhydrodicotarninetrinitromesitylene*.

All these condensations occur in accordance with the following scheme, in which the case of 2:4-dinitrotoluene is represented, and the intermediate phases, referred to later, are omitted:



The cyclic constitution assigned to these condensation products is justified in this particular instance by the results obtained in examining the exhaustive methylation of the base.

Anhydrocotarnine-2:4-dinitrotoluene methiodide (I) yields, by conversion into the methochloride and treatment with alkali, the *base* (II), which in turn yields a *methiodide*. The *methyl hydroxide* (III) corresponding with this salt possesses considerable stability, but is slowly decomposed on boiling with water, the products being trimethylamine and the neutral substance (IV). The constitution of this final product was proved by its synthesis from cotarnone and 2:4-dinitrotoluene (see p. 2131):

$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{matrix}CH(CH_2 \cdot C_6H_3(NO_2)_2)-NMe_2I \\ CH_2 \cdot CH_2 \qquad\qquad\qquad\quad\ \end{matrix} \qquad \text{(I.)}$$

$$C_8H_6O_3{<}\begin{matrix}CH{:}CH \cdot C_6H_3(NO_2)_2 \\ CH_2 \cdot CH_2 \cdot NMe_2\end{matrix} \qquad \text{(II.)}$$

$$C_8H_6O_3{<}\begin{matrix}CH{:}CH \cdot C_6H_3(NO_2)_2 \\ CH_2 \cdot CH_2 \cdot NMe_3 \cdot OH\end{matrix} \qquad \text{(III.)}$$

$$C_8H_6O_3{<}\begin{matrix}CH{:}CH \cdot C_6H_3(NO_2)_2 \\ CH{:}CH_2\end{matrix} \qquad \text{(IV.)}$$

The alternative view of the constitution of anhydrocotarnine-2:4-dinitrotoluene, namely:

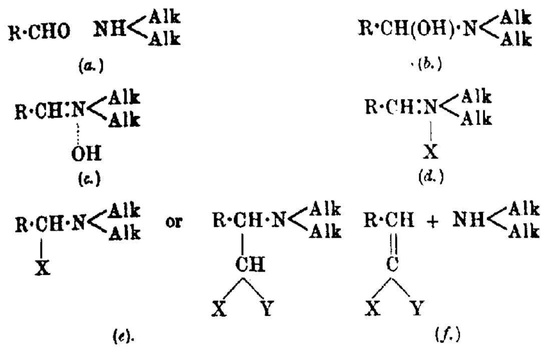
$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{matrix}CH{:}CH \cdot C_6H_3(NO_2)_2 \\ CH_2 \cdot CH_2 \cdot NHMe\end{matrix} \qquad \text{(A)}$$

is clearly proved to be incorrect, since the methiodide of the base correctly represented by the structure (I) is a quite different substance from the hydriodide of the stilbene derivative (II). There can be little doubt that the condensation products of cotarnine with other nitrotoluenes are also derivatives of benzylhydrocotarnine.

It is a matter of considerable interest that the bases produced from cotarnine and di- or tri-nitro-compounds are readily decomposed on boiling with glacial acetic acid, the original components being regenerated by the addition of a molecule of water. This hydrolysis can also be effected by alcoholic potassium hydroxide, and is probably not due to the intermediate formation of the open-chain substance (A), since the base (II) is not appreciably changed when boiled for an hour with acetic acid. The simplest scheme which represents the decomposition is the reverse of that formulated for the synthesis, but it may well be that the acid causes the group $\cdot CH_2 \cdot$ to migrate to the nitrogen, a process which it is clear would be at once followed by the formation of a cotarninium salt and a dinitrotoluene.

The Mechanism of the Condensation Reactions of Cotarnine and other Pseudo-bases.

Dr. Lapworth has suggested to the authors an explanation of the condensation of aldehydes and methylene compounds in the presence of a secondary base (Knoevenagel reaction), which may be represented as follows:



In the first stage free aldehyde (or ketone) and dialkylamine unite to form the carbinol (*b*), which is probably in all cases in equilibrium with the ammonium hydroxide (*c*). In ionising solvents, the equilibrium is naturally displaced in favour of this latter form.

The positive ion of (*c*) can unite with the negative residue of a substance H·X, where X is any group such as ·CN, $\cdot CH_2\cdot NO_2$, $\cdot CH_2\cdot C_6H_3(NO_2)_2$, $\cdot CH(CO_2Et)_2$, $\cdot CH_2\cdot COPh$, etc., and so produces the complex (*d*), which is very unstable, and changes to (*e*). When X is ·CN this represents the final stage, but in those cases where the substance H·X contains a reactive methylene group, that is, $CH_3\cdot X$ and CH_2XY, the further change to (*f*), with reproduction of the secondary base, occurs.

Finally, this unsaturated substance may add on another molecule of CH_2XY, a reaction completely analogous to the addition of ethyl sodiomalonate to $\alpha\beta$-unsaturated esters.

It is unnecessary to dilate on the probability of the above explanation, or to adduce specific chemical analogies for the various stages, but it may be stated that chemical literature contains experimental evidence for each of the changes involved. The spectroscopic investigations of Dobbie, Lauder, and Tinkler (Trans., 1903, **85**, 598) have clearly shown that cotarnine is an equilibrium mixture of carbinol (α) and ammonium hydroxide (β), the latter predomin-

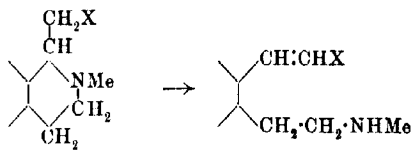
ating in alcoholic solution, whilst evidence for the open-chain aldehyde-imine structure is entirely lacking:,

$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{matrix}CH(OH)\cdot NMe\\ CH_2\text{——}CH_2\end{matrix} \quad \rightleftarrows$$
$$(\alpha.)$$

$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{matrix}CH{=}NMe\cdot OH\\ CH_2\cdot CH_2\end{matrix}$$
$$(\beta.)$$

The proved (β) structure of cotarnine in alcoholic solution corresponds with (c) in Lapworth's explanation of the Knoevenagel reaction, and the products of condensation with substances of the type H·X have been shown (see above) to possess a hydrocotarnine constitution, and to correspond therefore with (e). This explanation is consequently very simple in its application to the reactions of cotarnine,* requiring but one intermediate phase. The change (e) to (f) does not occur in the case of the majority of the condensation products of cotarnine, and the only example in which we suspect it is that of the condensation with dinitrophenylacetic ester (p. 2132), and even in this instance the evidence is very inconclusive.

With hydrocotarnine compounds the change in question is represented as follows:



The probable reason for the fact that unsaturated substances of this type are not produced must be sought in the stability of the ring structure.

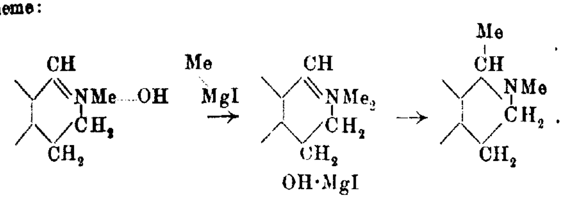
On the basis of the above hypothesis, cotarnine, and, indeed, all pseudo-bases, should condense with any substance which is capable of giving rise to a negative ion, unless the reaction is sterically hindered, or is in opposition to the laws of thermodynamics. Various considerations will, however, affect the stage which the resulting product reaches; thus, for example, with acids there is very little or no tendency for the acid radicle to migrate to carbon. Acid amides and imides are probably partly ionised in solution, and should therefore condense with cotarnine. In point of fact a number of substances described as molecular compounds of cotarnine and amides and imides have recently been produced (Knoll & Co.,

* Cotarnine is taken throughout this discussion as an example, but the observations are intended to apply to all pseudo-bases where there is a possibility of migration of groups from the nitrogen to carbon.

D.R.-P. 232785). We have examined one of them, namely, that from cotarnine and phthalimide, and our analysis proves that the substance is anhydrocotarninephthalimide, loss of water having occurred. Although this compound is immediately decomposed by acids with the production of cotarninium salts and phthalimide, we regard it as analogous to ethoxyhydrocotarnine, that is, as phthaloylaminohydrocotarnine.

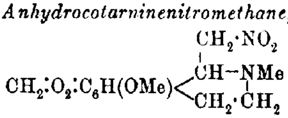
In those cases where an agent has been found necessary to effect the condensation of a pseudo-base with a third substance, this agent can have no effect on the base, except to suppress its ionisation and so hinder the reaction. The agent facilitates the condensation by enabling the third substance, most probably a feeble pseudo-acid, to give rise to a negative ion. The condensation of cotarnine with *o*- or *p*-nitrotoluene in the presence of sodium ethoxide (see p. 2123) probably belongs to this category.

In conclusion, it may be mentioned that the action of magnesium alkyl haloids on cotarnine and other pseudo-bases must probably be explained by a similar idea, which is expressed in the following scheme:



EXPERIMENTAL.

Anhydrocotarninenitromethane,



This substance is prepared with great facility according to the following method:

A solution of cotarnine (20 grams) in ethyl alcohol (40 c.c.) is mixed with nitromethane (15 grams), when the temperature rises, and in about half a minute the condensation product crystallises from the liquid. After remaining an hour at the room temperature, the crystals are separated and washed with alcohol, a further quantity being obtained from the mother liquors on standing for a few days. The substance is readily soluble in boiling ethyl alcohol, and crystallises on cooling in fine, colourless prisms, melting at 129°. On analysis of a specimen dried in a vacuum:

0·1191 gave 0·2441 CO_2 and 0·0588 H_2O. C=55·8; H=5·5.

$C_{13}H_{16}O_5N_2$ requires C=55·7; H=5·7 per cent.

A characteristic property of the substance is the formation of a very sparingly soluble hydrochloride. This crystallises in needles and can be dissolved in a large excess of water. No trace of a benzoyl derivative could be isolated, whether the benzoylation was carried out with benzoyl chloride in aqueous alkaline or pyridine solution.

Picrate:—The base was dissolved in acetic acid, and the solution diluted with water and treated with picric acid. The yellow precipitate was collected, and crystallised from a mixture of methyl ethyl ketone and ethyl alcohol. Long, bright yellow, slender needles were obtained, which melted at 136—137°. On analysis the substance exploded with violence in the tube, so that a high result was always obtained in a nitrogen determination.

Action of Methyl Iodide on Anhydrocotarninenitromethane.

The finely powdered substance was boiled with an excess of pure methyl iodide, when the colourless crystals were gradually replaced by a yellow gum. After three hours this transformation was complete, and the methyl iodide was removed by distillation. The gummy residue was completely dissolved in boiling methyl alcohol, and the deep yellow solution allowed to cool. A quantity of intensely yellow crystals separated, and these were collected and recrystallised from methyl alcohol. The melting point of this methiodide was 229°. A specimen that had been recrystallised five times was dried in a vacuum, and analysed:

0·1381 gave 0·2125 CO_2 and 0·0655 H_2O. C=41·9; H=5·3.
0·1178 „ 0·1800 CO_2 „ 0·0560 H_2O. C=41·7; H=5·3.
0·1221 „ 0·0659 AgI. I=29·2.

$C_{15}H_{21}O_5N_2I$ requires C=41·3; H=4·8; I=29·1 per cent.

These results show that this substance is probably a *methylanhydrocotarninenitromethane methiodide*, and has the constitution:

$$C_8H_6O_3<\begin{matrix}CH{:}CH\cdot NO_2\\ CH_2\cdot CH_2\cdot NMe_3I\end{matrix}.$$

Proof of the correctness of this view is afforded by the examination of the products of its decomposition with alkalis. The methiodide was converted into the corresponding methochloride in the usual way by heating with silver chloride in aqueous solution, and on the addition of potassium hydroxide, trimethylamine was very readily evolved. The solution was distilled, the distillate acidified with hydrochloric acid, concentrated, and treated with

platinic chloride, when a platinichloride was obtained, which melted at 238—239°, and possessed all the characteristics of trimethylamine platinichloride. We were unable to isolate the neutral decomposition product.

When the methiodide melting at 229° had been separated from the methyl-alcoholic mother liquor, another substance began to crystallise. It was at once obvious that this was a second methiodide, since it was only pale yellow in colour, and had a characteristic property of absorbing water of crystallisation. The substance was purified by many crystallisations from methyl alcohol, and was obtained in almost colourless, prismatic needles, which lose solvent of crystallisation at 110—115°, and then melt at 199°. The analytical results for this substance were unsatisfactory, since it loses some of its solvent of crystallisation on drying in the air. In order to obtain the percentage of iodine in the dry substance, determinations of the loss on heating and of the iodine were made with the same air-dried specimen:

0·7882 lost, at 120°, 0·0180 solvent. $CH_4O = 2·3$ per cent.

0·1253 gave 0·0681 AgI. $I = 30·0$ (calculated for anhydrous substance).

$C_{14}H_{19}O_5N_2I$ requires $I = 30·0$ per cent.

When a little of the substance is ground up with water, it swells up and becomes a mass of pale yellow needles. It was recrystallised from water, dried in air, and the loss on heating determined:

0·9774 lost 0·0516 H_2O. $H_2O = 5·2$.

$C_{14}H_{19}O_5N_2I,H_2O$ requires $H_2O = 4·1$ per cent.

The substance melted at 105—115°, then re-solidified, and melted at 196—198°. On decomposition of this methiodide with alkali practically no volatile base was obtained; it gave the merest trace of a platinichloride, melting at 228°.

All the above observations are in agreement with the hypothesis that this second methiodide is the normal methiodide of anhydrocotarninenitromethane. It can be represented by either of the following formulæ, but we prefer the first, and regard the production of the yellow methiodide as occurring by the opening of the isoquinoline ring:

$$C_8H_6O_3<\begin{matrix} CH_2\cdot NO_2 \\ | \\ CH-NMe_2I \\ | \\ CH_2\cdot CH_2 \end{matrix} \qquad C_8H_6O_3<\begin{matrix} CH{:}CH\cdot NO_2 \\ CH_2\cdot CH_2\cdot NMe_2HI \end{matrix}$$

(I.) (II.)

Further experiments have been made, and will be made, on this base, in respect, for example, of its reduction products, but it is hoped that they will form the subject-matter of a future communi-

cation. In the meantime we have represented the substance as a derivative of hydrocotarnine, the chief arguments in favour of this view being its lack of visible colour and the formation of a normal methiodide.

Anhydrocotarninenitroethane Methiodide,

$$CH_2{:}O_2{:}C_6H(OMe){<}\begin{array}{l}\quad CH_3\cdot CH\cdot NO_2 \\ CH{-}NMe_2I \\ CH_2\cdot CH_2\end{array}.$$

Cotarnine (6 grams) was dissolved in alcohol, and the solution boiled for ten minutes with nitroethane (1·9 grams). On evaporating a portion of the solution, a gummy residue was obtained, and this could not be induced to crystallise. That a condensation had occurred was proved by the following experiments. In the first place, a solution of the gum in dilute hydrochloric acid gave, on addition of picric acid, a bright yellow precipitate of a picrate, which crystallised from acetone in greenish-yellow prisms, melting at 114—116°. This could not be cotarnine picrate, and was therefore the picrate of a condensation product. The main portion of the gum was treated with boiling methyl iodide, when a methiodide was produced, and became solid in contact with cold methyl alcohol. After separation, the substance was crystallised from methyl alcohol, and was obtained in pale yellow, rectangular plates, melting and decomposing, with slight previous darkening, at 216—218°. This melting point led us to suspect that the substance was cotarnmethine methiodide, which melts at 217—219°; but a careful comparison of the two substances clearly proved that this was not the case; also, an intimate mixture of these methiodides melted at 196—200°.

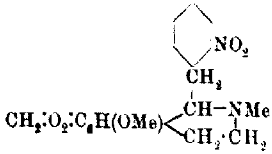
On analysis of a specimen dried in a vacuum:

0·1409 gave 0·0766 AgI. I = 29·4.

$C_{15}H_{21}O_5N_2I$ requires I = 29·1 per cent.

Since in the case of anhydrocotarninenitroethane only one methiodide is isolated, it probably corresponds with the simple methiodide of anhydrocotarninenitromethane, a supposition which is in agreement with its pale yellow colour and its percentage of iodine. The constitution of the substance is probably correctly represented at the head of the section, but it is impossible to be sure of this until the products of its decomposition by alkalis are examined. A volatile base is produced in only very small quantities in this reaction.

Anhydrocotarnine-2-nitrotoluene,



A condensation can be effected between cotarnine and *o*-nitrotoluene in the absence of any condensation agent, but the process is slow, and results in a small yield of the desired product. The use of sodium ethoxide was found to have a large effect in facilitating the preparation of this substance, and the following were the conditions employed:

A solution of sodium ethoxide (0·5 gram of sodium) in alcohol (50 c.c.) was added to a mixture of cotarnine (5 grams) and *o*-nitrotoluene (10 grams), and the liquid was then kept in the cold for twenty-four hours. The yellow solution was then treated with dilute hydrochloric acid, and extracted with ether to remove the excess of nitrotoluene. The aqueous layer was separated, and, after saturating with sodium acetate, again extracted with ether. In this way the condensation product is separated from cotarnine, because the latter is not liberated from its salts by sodium acetate.

The pale yellow ethereal solution was washed with water, dried with potassium carbonate, and distilled, leaving a viscid, yellow oil, which could not be induced to crystallise. It was dissolved in alcohol, and treated with a solution of picric acid in the same solvent, when after a short time a very sparingly soluble picrate crystallised from the solution in intense yellow prisms. The substance so obtained was quite pure, as the following analysis indicates, and very little is to be gained by the crystallisation of this picrate, since the only solvent in which it is sufficiently soluble for the purpose is acetic acid, and a certain amount of decomposition ensues. A specimen of this derivative was later prepared from the pure base, and found to melt at 203—205°:

0·1275 gave 12·7 c.c. N_2 at 14° and 752 mm. N = 11·5.

$C_{24}H_{21}O_{12}N_6$ requires N = 11·9 per cent.

The picrate was then decomposed by very dilute sodium hydroxide, whilst the base produced was simultaneously extracted with ether. This process was accomplished in a very much shorter time when the alkali was repeatedly changed. In any case, the picrate is difficult to decompose, especially by ammonia or potassium hydroxide.

The ethereal solution of anhydrocotarnine-2-nitrotoluene was washed with water, dried with potassium carbonate, and distilled. The residue now became solid on scratching the sides of the containing vessel, and the substance was twice recrystallised from not too much methyl alcohol. It was so obtained in pale yellow prisms, melting at 75°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1235 gave 0·2891 CO_2 and 0·0650 H_2O. C=63·8; H=5·8.

$C_{19}H_{20}O_5N_2$ requires C=64·0; H=5·6 per cent.

This compound is readily soluble in ethyl alcohol or ether, more sparingly so in methyl alcohol or light petroleum; from a hot solution in the latter solvent it is deposited in flat prisms, which are all but colourless.

The hydrochloride is sparingly soluble in water, and crystallises in perfectly colourless micro-prisms of rather indefinite shape, when the solution of the base in concentrated hydrochloric acid is diluted. The double salts, for example, the platinichloride, aurichloride, and mercurichloride, are very sparingly soluble amorphous precipitates. The substance dissolves readily in dilute sulphuric acid, but the sulphate soon crystallises from the solution, and consists of colourless, rectangular prisms.

When a warm solution of the hydrochloride is treated with zinc, reduction readily occurs, and the pale yellow liquid resulting on the addition of sodium nitrite contains a diazonium salt, which yields intense red azo-dyes with β-naphthol and "R-salt" in alkaline solution.

It is of interest to note that this base is not decomposed by boiling with acetic acid, and in this respect it differs from the dinitro-derivatives shortly to be described.

Anhydrocotarnine-4-nitrotoluene,

$$
\begin{array}{l}
\qquad\qquad\qquad\qquad\quad CH_2\cdot C_6H_4\cdot NO_2 \\
\qquad\qquad\qquad\qquad\quad | \\
CH_2{:}O_2{:}C_6H(OMe)<\begin{array}{l} CH-NMe \\ \qquad\;\; | \\ CH_2\cdot CH_2 \end{array}
\end{array}
$$

The experience gained in dealing with the foregoing substance was applied in condensing cotarnine with *p*-nitrotoluene, since it was found that the reaction was impracticably slow without a condensing agent.

A mixture of cotarnine (10 grams), *p*-nitrotoluene (15 grams), and alcohol (100 c.c. containing sodium ethoxide from 1 gram of sodium) was gently warmed until a clear solution was obtained, and then allowed to remain without further heating for a day. The liquid was diluted with water, acidified with hydrochloric acid, and

eparated by filtration from the unchanged *p*-nitrotoluene. The ddition of ammonia to the filtrate produced a milky solution, from which a quantity of a crystalline substance gradually separated. This was collected, and crystallised, first from methyl, and then rom ethyl alcohol.

On analysis of a specimen dried in a vacuum over sulphuric acid:

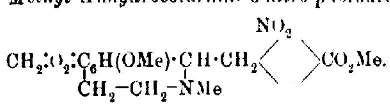
0·1331 gave 0·3138 CO_2 and 0·0711 H_2O. C = 64·3; H = 5·9.

$C_{19}H_{20}O_5N_2$ requires C = 64·0; H = 5·6 per cent.

Anhydrocotarnine-4-nitrotoluene is readily soluble in boiling ethyl alcohol, but sparingly so in the cold, and separates in aggregates of leaf-shaped crystals. It melts at 121—122°, without decomposition. Although it is a pale yellow substance, it forms colourless salts, of which the hydrochloride and sulphate are sparingly soluble in water, the former crystallising from a hot aqueous solution in glistening, elongated prisms. The platinichloride is an amorphous precipitate, which changes to yellow needles on boiling the solution. A *picrate* very sparingly soluble in alcohol is produced in canary-yellow prisms when picric acid is added to a hot alcoholic solution of the base. This derivative melts at 188—190°.

The observations on the stability in boiling acetic acid and on the formation of azo-dyes that were made with anhydrocotarnine-*p*-nitrotoluene (see above), apply also to anhydrocotarnine-4-nitrotoluene.

Methyl Anhydrocotarnine-o-nitro-p-toluate,



Methyl *o*-nitro-*p*-toluate is mentioned by Noad (*Annalen*, 1847, 63, 297), who describes it as a crystalline substance. We have prepared it by boiling *o*-nitro-*p*-toluic acid with 5 per cent. methyl-alcoholic sulphuric acid for half an hour. The ester crystallises well from methyl alcohol in long, colourless needles, and melts sharply at 81°:

0·1130 gave 0·2282 CO_2 and 0·0478 H_2O. C = 55·1; H = 4·7.

$C_9H_9O_4N$ requires C = 55·4; H = 4·6 per cent.

Although it is a mononitrotoluene derivative, the negative effect of the carbomethoxy-group is so great that the condensation with cotarnine can be accomplished without the use of sodium ethoxide. In carrying out this reaction a solution of methyl *o*-nitro-*p*-toluate (10 grams) and cotarnine (10 grams) in methyl alcohol (65 c.c.) was boiled for three hours. The solution was then cooled, and allowed to remain in the ice-chest overnight. The substance gradually crystallised from the yellowish-brown liquid, and very

little of the base remained in the mother liquor. It was collected, washed with methyl alcohol, dried, and crystallised by adding methyl alcohol, in which it is very sparingly soluble, to its saturated solution in boiling methyl ethyl ketone. Almost colourless, prismatic crystals were obtained, and after recrystallisation melted at 146-

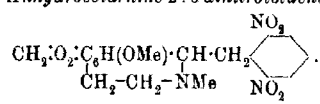
0·1500 gave 0·3360 CO_2 and 0·0741 H_2O. C = 61·1; H = 5·5.

$C_{21}H_{22}O_7N_2$ requires C = 60·9; H = 5·3 per cent.

The substance yields readily soluble salts with mineral acids, and the usual not very characteristic, sparingly soluble double salts. I is not changed on boiling with glacial acetic acid for a short time. The picrate is obtained in canary-yellow prisms, melting a 163—170°, by adding a methyl-alcoholic solution of picric acid to solution of the base in methyl ethyl ketone.

When the base is boiled with alcoholic potassium hydroxide gradually dissolves, and is not reprecipitated on the addition o water. That the ester has been hydrolysed in a normal manner is proved by the fact that on the addition of hydrochloric acid and aqueous picric acid to the solution a bright yellow picrate is precipitated. This can be recrystallised from a large quantity of a mixture of equal parts of acetone and methyl alcohol, and occurs in microscopic prisms, melting at 183—185°. Its formulation as anhydrocotarnine-o-nitro-p-toluic acid picrate is justified by its immediate and complete solubility in sodium carbonate, and by the conversion into methyl anhydrocotarnine-o-nitro-p-toluate picrate, a change which can be effected by the agency of a solution of picric acid in methyl-alcoholic hydrochloric acid. The melting point of the picrate falls to 168° with slight previous softening, it is no longer soluble in sodium carbonate, and on treatment with alkali and ether is decomposed, so that the original ester base can be recovered from the ethereal solution.

Anhydrocotarnine-2:6-dinitrotoluene,



A solution of 2:6-dinitrotoluene (3·6 grams) in as little methyl alcohol as possible was added to cotarnine (4·8 grams) and methyl alcohol (30 c.c.), and the mixture boiled for five minutes. After some time the deep brownish-red solution began to deposit a crystalline substance. In subsequent operations this separation was very much facilitated by seeding. The crystals were collected, washed with methyl alcohol, and recrystallised from ethyl alcohol. The methyl-alcoholic mother liquor and washings contain a further

quantity of the substance, which can be obtained by the partial evaporation of the solvent. The new substance crystallises from ethyl alcohol in bright yellow prisms, melting at 112—114°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1347 gave 0·2824 CO_2 and 0·0578 H_2O. C = 57·2; H = 4·8.

$C_{19}H_{19}O_7N_3$ requires C = 56·8, H = 4·7 per cent.

The substance is readily soluble in boiling ethyl alcohol and in chloroform or benzene. When boiled with acetic acid, the colourless solution becomes yellow, and 2 : 6-dinitrotoluene (m. p. 60°) and cotarnine acetate are produced.

The *picrate* is obtained by mixing a solution of the base in methyl ethyl ketone with an alcoholic solution of picric acid. It is sparingly soluble in most solvents, and forms canary-yellow prisms, melting at 153—155°.

Methiodide.—The base was boiled with an excess of methyl iodide for ten minutes, when a methiodide was produced, which crystallised from methyl alcohol in light yellow prisms, melting at 210—212°. Although the substance had all the characteristics of a pure compound, and its melting point was not raised by further crystallisation, yet, as the following results show, the percentage of iodine found was always high:

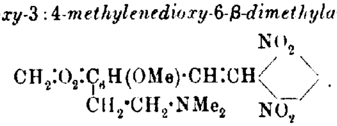
0·1390 gave 0·0627 AgI. I = 24·4.

0·1215 „ 0·0562 AgI. I = 25·0.

$C_{20}H_{22}O_7N_3I$ requires I = 23·4 per cent.

We are unable to suggest any explanation of this anomaly, since we regard the constitution of the substance as proved by its decomposition with alkalis, as described in the next section.

2′ : 6′-Dinitro-2-methoxy-3 : 4-methylenedioxy-6-β-dimethylamino-ethylstilbene,



Anhydrocotarnine-2 : 6-dinitrotoluene methiodide was dissolved in hot water, and heated on the steam-bath with an excess of freshly precipitated silver chloride during a quarter of an hour. Silver iodide was produced, and the solution of the methochloride was collected and treated with excess of sodium hydroxide. After gently warming for a few minutes, the copious, brown precipitate which was formed was collected, washed, dried, and crystallised from methyl alcohol.

When prepared in this way the substance has a brilliant, orange-red colour, and occurs in lozenge-shaped plates, melting at 93—95°,

but occasionally yellow crystals melting at 75° were obtained; these contained solvent of crystallisation, and on remaining overnight in the air, reverted to the red variety, and melted at 94°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

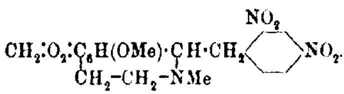
0·1200 gave 0·2568 CO_2 and 0·0551 H_2O. C=58·3; H=5·1.

$C_{20}H_{21}O_7N_3$ requires C=57·8; H=5·0 per cent.

Considerable care was necessary in carrying out the combustion, as the compound tends to decompose with violence.

This substance is a base entirely analogous to the corresponding compound from 2:4-dinitrotoluene. It is sparingly soluble in cold methyl alcohol, but readily soluble in ethyl acetate or benzene. The hydrochloride is sparingly soluble in water or cold alcohol, readily in boiling alcohol, and on the addition of picric acid to the solution a crystalline picrate is obtained.

Anhydrocotarnine-2:4-dinitrotoluene,



This substance was prepared in a manner exactly similar to that described in the case of the 2:6-isomeride (see above), but it was obtained with greater readiness, and in practically quantitative yield.

When equimolecular quantities of cotarnine and 2:4-dinitrotoluene were boiled together in methyl-alcoholic solution, separation of the yellow crystals of the condensation product usually occurred in a few minutes, and while the liquid was hot. The crystalline precipitate was separated from the cooled solution by filtration, and the substance purified by crystallisation from a mixture of chloroform and methyl alcohol. The yellow prisms so obtained melt at 145—146° with vigorous decomposition.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1194 gave 0·2477 CO_2 and 0·0518 H_2O. C=56·6; H=4·8.

$C_{19}H_{19}O_7N_3$ requires C=56·8; H=4·7 per cent.

The substance is sparingly soluble in methyl or ethyl alcohol and in benzene, readily so in chloroform or pyridine. The base itself and all its derivatives are more sparingly soluble than the corresponding isomerides from 2:6-dinitrotoluene.

The solution of the compound in dilute hydrochloric acid is pale yellow, and the addition of ammonia regenerates the unchanged substance as a light yellow, amorphous precipitate, rapidly becoming crystalline. The same applies to the solution of the base in cold

acetic acid; if, however, this solution is boiled, then decomposition ensues, with production of cotarnine (picrate, m. p. 141—143°) and dinitrotoluene (m. p. 69°). This decomposition is discussed in the introduction to the paper.

Precipitates of double salts are obtained when the appropriate reagents are added to a solution of the base in dilute acid, but they are not specially characteristic.

Methiodide.—This derivative was obtained by boiling the finely powdered substance with an excess of methyl iodide. The salt was quickly formed, and was found to crystallise from methyl alcohol in orange prisms. If quickly heated the substance will melt and evolve gas, even below 180°, but when the melting point is taken slowly it is found to be 244—245°, with gradual decomposition above 200°. Great difficulty was experienced in obtaining a pure specimen of this methiodide, although, as in the case of the 2:6-dinitro-compound, the external characteristics were those of a single substance:

0·1748 gave 0·0738 AgI. I = 22·8.

$C_{20}H_{22}O_7N_3I$ requires I = 23·4 per cent.

2′:4′-Dinitro-2-methoxy-3:4-methylenedioxy-6-β-dimethylaminoethylstilbene, $C_8H_6O_3{<}^{CH:CH\cdot C_6H_3(NO_2)_2}_{CH_2\cdot CH_2\cdot NMe_2}$.

The methiodide of anhydrocotarnine-2:4-dinitrotoluene was converted into the methochloride by warming with silver chloride in aqueous solution, and after filtration an excess of sodium hydroxide was added. The dense, orange-coloured precipitate was collected, dried, and crystallised from ethyl acetate. It separates in long, reddish-brown prisms, melting at 155°.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1335 gave 0·2833 CO_2 and 0·0656 H_2O. C = 57·8; H = 5·4.

0·1145 „ 0·2440 CO_2 „ 0·0500 H_2O. C = 58·1; H = 4·8.

$C_{20}H_{21}O_7N_3$ requires C = 57·8; H = 5·0 per cent.

This substance is very sparingly soluble in hot methyl alcohol, but easily dissolves in boiling chloroform or ethyl acetate. The hydrochloride is very sparingly soluble in water and alcohol; it crystallises from aqueous alcohol in yellow plates. A hot aqueous-alcoholic solution of the hydrochloride on treatment with picric acid deposits lozenge-shaped crystals of a yellow picrate, which melt at 185—187°.

Hydriodide.—This derivative is of considerable interest in that the fact of its difference from the methiodide of anhydrocotarnine-2:4-dinitrotoluene proves that the latter base has a hydrocotarnine

structure. It is obtained as a yellow precipitate by mixing a solution of the base in glacial acetic acid with a dilute alcoholic solution of hydriodic acid, and the yellow crystals on boiling with alcohol are converted into brilliant red prisms. The substance was crystallised from formic acid, and separated at first as the red variety, which could be obtained in a pure condition. When, however, a certain temperature was reached, the yellow form began to crystallise in glistening flakes. It appears that the yellow form separates at low temperatures, and it can always be converted into the more stable red form by warming in the presence of any solvent in which the substance is partly soluble. The yellow crystals were not obtained free from the red; the latter melt and decompose at 245—248°, and gave the following result on analysis:

0·1166 gave 0·0498 AgI. I = 23·1.

$C_{20}H_{22}O_7N_3I$ requires I = 23·4 per cent.

Methiodide.—When the base is boiled for five minutes with methyl iodide a methiodide is produced, which is exceedingly sparingly soluble in almost all solvents. The substance was prepared in considerable quantity, and purified by extraction with boiling ethyl acetate which removed any unaltered base. For analysis a small specimen was obtained in a pure condition by crystallisation from a large quantity of methyl alcohol. It consists of orange-yellow, rectangular prisms, which melt at 244—246°:

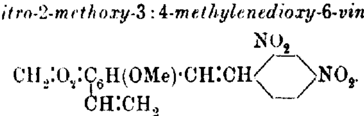
0·1575 gave 0·0661 AgI. I = 22·7.

$C_{21}H_{24}O_7N_3I$ requires I = 22·8 per cent.

The corresponding *methochloride* was produced by heating this methiodide in aqueous suspension with freshly precipitated silver chloride. The filtered solution deposits on cooling a crystalline precipitate resembling very much lead iodide. The methochloride, although, as is usual, more soluble than the methiodide, is still sparingly soluble in water and alcohol. It is stable in the presence of alkaline hydroxides, so that it was necessary to resort to the use of silver oxide in order to obtain the quaternary ammonium base.

In the experiment which is described below, it was found to be more convenient to employ the methiodide direct.

2′:4′-Dinitro-2-methoxy-3:4-methylenedioxy-6-vinylstilbene.



The methiodide described above (5 grams) was completely dissolved in the least possible quantity of hot water (5 litres), and

digested on the steam-bath with silver oxide (from 10 grams of silver nitrate) during six hours. The orange-coloured solution was filtered, and evaporated until crystallisation at the surface commenced. The solution had the odour of trimethylamine, and was filtered from a small quantity of a neutral, red substance. On cooling, a new substance crystallised in golden spangles, which under the microscope are seen to consist of irregular, hexagonal prisms. On heating, the compound turns red at 120—130°, and then decomposes at 164—166°. Its whole behaviour harmonises with the view that it is a methyl hydroxide, and one which evidently possesses considerable stability. It dissolves in hot water, and the yellow solution gives a precipitate of the characteristic methochloride with hydrochloric acid. The stability of this ammonium base is remarkable, and we experienced great difficulty in causing its fission into trimethylamine and the neutral stilbene derivative. This could be accomplished, at the expense of great loss through decomposition, by heating the substance in the dry state. The method finally adopted was to boil a concentrated aqueous solution for many hours, when a slow decomposition occurred, involving the production of trimethylamine and a red powder, which was separated by filtration. The substance was purified by boiling with water to remove a small quantity of unaltered methyl hydroxide, and, after drying, crystallised from acetone. The crystals are tiny, rectangular prisms, melting at 162—163°. When first obtained they are brownish-yellow, but on drying at 90° they become deep, brilliant red. The substance is quite devoid of basic properties, and crystallises unchanged from acetic acid. It is fairly soluble in hot acetone, and sparingly so in alcohol.

On analysis of a specimen dried at 90°:

0·1173 gave 0·2535 CO_2 and 0·0441 H_2O. C = 58·9; H = 4·2.

$C_{18}H_{14}O_7N_2$ requires C = 58·4; H = 3·8 per cent.

In order to be quite sure of the constitution of this neutral substance, its synthesis was accomplished by the following process:

Cotarnone (2 grams) and 2:4-dinitrotoluene (2 grams) were melted together, and warmed on the water-bath for an hour with three drops of piperidine. The mass of red crystals which resulted was dissolved in boiling acetic acid, and on cooling the substance separated in aggregates of micro-prisms, resembling chromic acid in appearance. The substance melted, after recrystallisation, at 163—164°, and its melting point was unaltered by admixture with the substance obtained as above from anhydrocotarninedinitrotoluene:

0·1409 gave 0·3040 CO_2 and 0·0497 H_2O. C = 58·8; H = 3·9 per cent.

Methyl Anhydrocotarnine-2:4-dinitrophenylacetate,

$$CH_2{:}O_2{:}C_6H(OMe)\cdot CH{:}C(CO_2Me)\cdot C_6H_3(NO_2)_2 \quad (1).$$
$$CH_2\cdot CH_2\cdot NHMe$$

This substance was prepared by the condensation of methyl dinitrophenylacetate (Borsche, *Ber.*, 1909, **42**, 1310) with cotarnine under the following conditions. A mixture of the ester (2 grams) and an equal quantity of cotarnine was boiled for five minutes with enough methyl alcohol to dissolve it. The solution acquires a deep black colour, and on cooling deposits jet black crystals, which were collected and dried. The substance was recrystallised from methyl alcohol, and obtained in black prisms, which show green iridescence and melt at 150—151° with vigorous decomposition.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1310 gave 0·2649 CO_2 and 0·0561 H_2O. C=55·1; H=4·7.
$C_{21}H_{21}O_9N_3$ requires C=54·9; H=4·5 per cent.

The black colour of this substance, which is so characteristic, is only observed in the crystalline condition; when rubbed on paper, a brown streak is produced, and cold methyl alcohol is coloured red by contact with the solid. No stable salts could be prepared, since in contact with strong or dilute acids it is at once decomposed with production of cotarnine and of methyl dinitrophenylacetate (m. p. 82°). Further, as seen below, no methiodide could be obtained. It is in consideration of these facts, which clearly show its lack of resemblance to anhydrocotarnine-2:4-dinitrotoluene, that we have assigned the open-chain structure, figured above, to this substance.

Action of Methyl Iodide.—The black condensation product was boiled for an hour with an excess of methyl alcohol and methyl iodide. On cooling, a quantity of reddish-brown crystals were obtained, and these were collected, drained on porous porcelain, and recrystallised from methyl alcohol. The faintly yellow crystals were examined under the microscope, and found to consist of hexagonal plates, and no crystals of other shape could be detected. The melting point was 210—213° (decomp.), and was unaltered by the recrystallisation of the substance. It is evidently a pure compound, but we have been unable to identify it. The percentage of iodine found was 35·5, which is much too high for the normal methiodide (21·1), and agrees better for a substance like hydrocotarnine methiodide or hydriodide. These compounds were prepared in order to effect a direct comparison, but the result showed that the unidentified methiodide was a different substance.

Hydrocotarnine Hydriodide.—This salt was prepared by the addition of concentrated aqueous hydriodic acid to a solution of

hydrocotarnine in alcohol. The substance crystallises from methyl alcohol in colourless needles, melting at 195—196°.

Hydrocotarnine Methiodide.—Hydrocotarnine reacts with methyl iodide in the cold, and the product crystallises well from methyl alcohol in magnificent prisms. This derivative melts without decomposition at 206—207°.

On analysis of a specimen dried in a vacuum:

0·1009 gave 0·0650 AgI. I = 34·8.

$C_{13}H_{18}O_3NI$ requires I = 35·0 per cent.

Anhydrocotarnine-2:4:6-trinitrotoluene,

$$CH_2{:}O_2{:}C_6H(OMe)\cdot\underset{\textstyle CH_2-CH_2-NMe}{CH\cdot CH_2\cdot C_6H_2(NO_2)_3}.$$

Cotarnine condenses with trinitrotoluene as readily as with nitromethane, and the preparation of the condensation product is a very simple matter, and merely consists in grinding up trinitrotoluene with an alcoholic solution of an equimolecular quantity of cotarnine. As soon as the substances come into contact, the orange-yellow compound commences to crystallise, and the reaction is complete in a few minutes. The crystals are collected, and dissolved in cold chloroform, and, on adding methyl alcohol to the solution, the new compound is obtained in a pure condition as intense yellow prisms, melting, when slowly heated, at 130° with explosive decomposition. This property rendered the analysis of the substance a matter of some difficulty, and high results were obtained, both for carbon and hydrogen. This could scarcely be avoided, since even when the substance was mixed with a large excess of copper oxide an explosion occurred, and nitrous fumes could be seen in the bulbs.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1224 gave 0·2321 CO_2 and 0·0517 H_2O. C = 51·7; H = 4·7.

$C_{19}H_{18}O_9N_4$ requires C = 51·1; H = 4·0 per cent.

The substance is sparingly soluble in most neutral solvents, but readily dissolves in cold chloroform, giving a brownish-yellow solution. The solutions in hot alcohol or ethyl acetate are, however, intensely red, and this property is so characteristic that although the trinitro-compound is practically insoluble, yet alcohol is coloured red by contact with it in the cold.

The base dissolves in concentrated hydrochloric acid, forming a pale yellow solution, which remains clear on dilution with water; on keeping, however, long, yellow needles of the hydrochloride crystallise out, and may be recrystallised from warm dilute hydrochloric acid. If the solution of the hydrochloride is boiled, trinitrotoluene is obtained, but the process is not a smooth one. When

the pale yellow solution of the base in glacial acetic acid is boiled, a complete decomposition ensues, with the production of trinitrotoluene and cotarnine. The former crystallised from the acetic acid solution in needles melting at 81°, whilst the latter was obtained in the form of its picrate (m. p. 141—143°) when the diluted and filtered mother liquor from this crystallisation was treated with picric acid.

Dianhydrodicotarnine-2 : 4 : 6-trinitro-m-xylene,

$$\underset{\displaystyle CH_2-CH_2-NMe}{CH_2{:}O_2{:}C_6H(OMe)\cdot CH}\cdot CH_2\cdot C_6H(NO_2)_3\cdot CH_2\cdot \underset{\displaystyle NMe\cdot C_2H_4}{CH-C_6H(OMe){:}O_2{:}CH_2}$$

Cotarnine was condensed with trinitro-*m*-xylene under the following conditions: Finely powdered trinitro-*m*-xylene (10 grams) was boiled with methyl alcohol (300 c.c.) sufficiently long to dissolve the greatest possible amount of the substance, and then treated with cotarnine (20 grams) and boiled for a further ten minutes. The trinitro-compound gradually passed into solution, and when the brownish-red liquid was allowed to remain in the cold a quantity of crystals separated. These were collected and recrystallised from ethyl acetate, and then again by adding methyl alcohol to the solution of the substance in a little cold chloroform. Pale yellow prisms of rather indefinite shape were obtained. The substance melts at 153—154° with vigorous decomposition and slight previous darkening.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1270 gave 0·2660 CO_2 and 0·0630 H_2O. C = 57·1; H = 5·5.

$C_{32}H_{33}O_{12}N_5$ requires C = 56·5; H = 5·0 per cent.

The rather high results that were obtained in this analysis do not militate against the conclusions we have drawn with respect to its composition, since they were certainly due to the same cause as in the case of the substance from trinitrotoluene. The substance closely resembles the compound produced by the condensation of trinitromesitylene and cotarnine, which from an analytical point of view was very carefully investigated (see p. 2135).

Dianhydrodicotarninetrinitro-m-xylene is a base readily soluble in dilute acids, but does not form any very characteristic derivatives. The platinichloride and aurichloride are amorphous precipitates. When the almost colourless solution of the base in glacial acetic acid is boiled, it acquires a yellow colour, and, on cooling, colourless prisms of trinitroxylene separate. The filtrate from these crystals (which melted at 182°) gives on dilution and treatment with picric acid a yellow precipitate of a picrate, which crystallises from alcohol or water in silky needles, melting at 139—143°, and obviously consists of the picrate of cotarnine.

Dianhydrodicotarninetrinitromesitylene,

$$C_6Me(NO_2)_3<\begin{matrix}CH_2\cdot C_{12}H_{14}O_3N\\ CH_2\cdot C_{12}H_{14}O_3N\end{matrix}$$

In order to effect a condensation between cotarnine and trinitromesitylene, it is not sufficient to boil an alcoholic solution of these substances on the steam-bath; much more vigorous treatment is necessary. The reaction was carried out as follows:

Trinitromesitylene (1·5 grams) was added to a solution of cotarnine (2 grams) in methyl alcohol (10 c.c.). The mixture was boiled as vigorously as possible in a test-tube, and continuously stirred with a glass rod, while the alcohol was allowed to evaporate. The trinitro-compound gradually dissolved, and a stage was reached at which the whole of it had passed into solution. The boiling was continued for one or two minutes longer, and the liquid was then poured into cold water. A pale yellow solid, at first rather viscid, was precipitated. Several such experiments were carried out, and the combined products separated by filtration and treated with dilute hydrochloric acid, which dissolved the greater part of the solid, forming a soluble salt, and leaving undissolved a small quantity of trinitromesitylene, which was removed by filtration. The yellow solution was rendered alkaline with ammonia, and the crude precipitated base was separated, washed, dried, and crystallised from a mixture of acetone and methyl alcohol. After four crystallisations the substance was obtained in pale yellow, prismatic crystals, melting at 183—185°. This crystallisation is very wasteful, and most of the analyses were made of specimens having rather lower melting point; indeed, the slightly impure substance melts so sharply at 175—176° that we had at first assigned this melting point to the compound.

On analyses of specimens dried in a vacuum over sulphuric acid:

A. 0·1429 gave 0·2993 CO_2 and 0·0695 H_2O. C = 57·1; H = 5·4.
B. 0·1273 „ 0·2683 CO_2 „ 0·0640 H_2O. C = 57·4; H = 5·5.
C. 0·0675 „ 6·15 c.c. N_2 at 17° and 755 mm. N = 10·4.
D. In a determination of methoxyl by Perkin's modification of Zeisel's method, 0·1910 gave 0·1211 AgI. MeO = 8·4.

$C_{33}H_{35}O_{12}N_5$ requires C = 57·1; H = 5·0; N = 10·0; MeO = 8·9 per cent.

(A) melted at about 168°; (B) was recrystallised (A), and melted at 171°; (C) was the purest specimen, melting at 183—185°; (D) melted at 175—176°. This substance was also prepared, using ethyl alcohol as the solvent, in which the reaction was carried out. The product obtained was identical with that described above; it melted at 175—177°, and the melting point was not lowered when the

substance was mixed with an equal quantity of the compound produced in the reaction when methyl alcohol was employed as solvent:

0·1218 gave 0·2552 CO_2 and 0·0589 H_2O. C=57·1; H=5·3.

This result of of interest, inasmuch as the analytical results for the base seemed to agree fairly well with the theory that one molecule of cotarnine condenses with one of the trinitro-compound, and that one of the nitro-groups is replaced by methoxyl. That this is not the case is shown by the above experiment.

The salts of this substance are readily soluble in water, and the solutions are almost colourless. On boiling with glacial acetic acid, trinitromesitylene (m. p. 228°) was obtained, the reaction evidently being quite analogous to the similar decomposition of anhydrocotarninetrinitrotoluene.

Anhydrohydrastininenitromethane,

$$\begin{array}{l} CH_2{:}O_2{\cdot}C_6H_2\text{——}CH{\cdot}CH_2{\cdot}NO_2 \\ \quad\quad\quad\quad\; CH_2{\cdot}CH_2{\cdot}NMe \end{array}$$

This substance, and also the condensation product with 2:4-dinitrotoluene, described in the next section, were prepared in order to show that hydrastinine is apparently as reactive as cotarnine towards nitro-compounds. Hydrastinine (1 gram) dissolved in methyl alcohol (5 c.c.) was treated with nitromethane (1 gram), and the solution boiled for one minute. On cooling, the substance separated in long, colourless needles, and was recrystallised from ethyl alcohol, in which it is sparingly soluble in the cold.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1220 gave 0·2567 CO_2 and 0·0650 H_2O. C=56·9; H=5·9.

$C_{12}H_{14}O_4N_2$ requires C=57·6; H=5·6 per cent.

The substance melts to a clear liquid at 121—122°. It is readily soluble in cold benzene or chloroform, less readily in ether. In contradistinction to the corresponding cotarnine compound, the hydrochloride is readily soluble in water; the dilute solution shows faint, bluish-green fluorescence. The aurichloride is an amorphous, light brown precipitate, soluble in hot alcohol, but separates in an oily condition on cooling.

An orange-yellow *picrate* separates in prismatic needles, melting at 173—174° on mixing hot alcoholic solutions of the base and picric acid.

Anhydrohydrastinine-2 : 4-dinitrotoluene,

$$CH_2{:}O_2{:}C_6H_2\text{——}CH{\cdot}CH_2{\cdot}C_6H_3(NO_2)_2$$
$$CH_2{\cdot}CH_2{\cdot}NMe$$

Hydrastinine (2 grams) and 2 : 4-dinitrotoluene (2 grams) were dissolved in boiling methyl alcohol (30 c.c.), and the solution boiled until the yellow, granular precipitate began to separate. After cooling, the substance was collected and recrystallised from a mixture of benzene and methyl alcohol. The yield approximated closely to that demanded by theory.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1201 gave 0·2568 CO_2 and 0·0482 H_2O. C = 58·3; H = 4·4.

$C_{18}H_{17}O_6N_3$ requires C = 58·2; H = 4·6 per cent.

The substance crystallises in microscopic balls of needles, is pale yellow, and melts at 143—144° with vigorous decomposition at a slightly higher temperature. It is very sparingly soluble in hot or cold alcohol, but readily so in benzene.

The *hydrochloride* is sparingly soluble in cold water, and can be crystallised from hot dilute hydrochloric acid. It forms pale yellow prisms.

The *picrate* is best prepared by mixing a hot solution of the base in methyl ethyl ketone with a solution of picric acid in the same solvent. It forms pale yellow prisms, melting at 172—173°, and is very sparingly soluble in the usual solvents.

The decomposition of this substance on boiling with acetic acid is quite similar to that of anhydrocotarnine-2 : 4-dinitrotoluene. The almost colourless solution of the base in glacial acetic acid acquires a yellow colour on boiling, and on dilution with water, needles, melting at 68° and consisting of dinitrotoluene, separate from the solution. The filtrate from these exhibits a strong bluish-green fluorescence showing the presence of hydrastinine.

In conclusion, we desire to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the expenses of this investigation.

THE UNIVERSITY,
MANCHESTER.

CONTENTS.

PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

ABSTRACTS OF PAPERS PUBLISHED IN OTHER JOURNALS:—

PART I.

Organic Chemistry.

PART II.

General and Physical Chemistry.

Inorganic Chemistry.

Mineralogical Chemistry.

Physiological Chemistry.

Chemistry of Vegetable Physiology and Agriculture.

Analytical Chemistry.

INDEX OF AUTHORS' NAMES

IN TRANSACTIONS AND ABSTRACTS

C.

D.

ERRATA.

Vol. LXXXVI (Abstr., 1904).

Part I.

Page.	Line.	
561	9*	for "Malonobenzylamic" read "Malobenzylamic
	6*	
	4*	
	1*	
562	3	
	5	
	6	

Vol. XCIX (Trans., 1911).

1907	16	*delete* "normal."
1909	5*	*insert* "$\rightleftharpoons$" in equation.
1948	18	*for* "quinoid" *read* "quinonoid."
2094	7	*for* "colourless" *read* "coloured."

* From bottom.

Anhydrohydrastinine-2:4-dinitrotoluene,

$$CH_2{:}O_2{:}C_6H_2\!\!-\!\!\!\underset{|}{-}\!CH\cdot CH_2\cdot C_6H_3(NO_2)_2$$
$$CH_2\cdot CH_2\cdot NMe$$

Hydrastinine (2 grams) and 2:4-dinitrotoluene (2 grams) were issolved in boiling methyl alcohol (30 c.c.), and the solution boiled ntil the yellow, granular precipitate began to separate. After oling, the substance was collected and recrystallised from a ixture of benzene and methyl alcohol. The yield approximated osely to that demanded by theory.

On analysis of a specimen dried in a vacuum over sulphuric acid:

0·1201 gave 0·2568 CO_2 and 0·0482 H_2O. C = 58·3; H = 4·4.

$C_{18}H_{17}O_6N_3$ requires C = 58·2; H = 4·6 per cent.

The substance crystallises in microscopic balls of needles, is pale llow, and melts at 143—144° with vigorous decomposition at a ightly higher temperature. It is very sparingly soluble in hot or ld alcohol, but readily so in benzene.

The *hydrochloride* is sparingly soluble in cold water, and can be ystallised from hot dilute hydrochloric acid. It forms pale llow prisms.

The *picrate* is best prepared by mixing a hot solution of the base methyl ethyl ketone with a solution of picric acid in the same lvent. It forms pale yellow prisms, melting at 172—173°, and very sparingly soluble in the usual solvents.

The decomposition of this substance on boiling with acetic acid quite similar to that of anhydrocotarnine-2:4-dinitrotoluene. The most colourless solution of the base in glacial acetic acid acquires yellow colour on boiling, and on dilution with water, needles, elting at 68° and consisting of dinitrotoluene, separate from the lution. The filtrate from these exhibits a strong bluish-green iorescence showing the presence of hydrastinine.

In conclusion, we desire to thank the Research Fund Committee the Chemical Society for a grant which has partly defrayed the penses of this investigation.

THE UNIVERSITY,
MANCHESTER.

CCXLI.—*The Electrochemistry of Solutions in Acetone. Part I.*

By ALEXANDER ROSHDESTWENSKY and WILLIAM CUDMORE McCULLAGH LEWIS.

WHILST a considerable amount of attention has been directed to the electrochemical behaviour of methyl and ethyl alcohols, relatively few measurements are recorded in the case of solutions in acetone. The present paper contains the results of an investigation undertaken to supply to a certain extent this deficiency. The solutes employed were lithium nitrate and silver nitrate, the latter being examined in greater detail. Before giving our own measurements, it is necessary to indicate briefly some of the results obtained by other observers which bear directly on the results obtained by us.*

As regards the electrolysis of saturated silver nitrate solutions in acetone, Kahlenberg (*J. physical Chem.*, 1900, **4**, 349) found that the metal was precipitated in a coherent form, but "the solution conducts so poorly" that it was impossible to verify Faraday's law. In the same paper Kahlenberg gives some results of electromotive force measurements of $Ag|AgNO_3$ concentration cells in pyridine and acetonitrile respectively, with regard to which he concludes that the Nernst expressions are inapplicable. Kahlenberg assumes that the liquid/liquid potential difference is negligible, which, in the case of acetone at least, we shall show later is not the case.

The specific conductivity of acetone itself has been measured by Dutoit and Levier (*J. Chim. phys.*, 1905, **3**, 435), the value obtained being $(2-0{\cdot}48)\times10^{-7}$ mho at the ordinary temperature (using unplatinised platinum electrodes). H. C. Jones and C. A. Rouiller (*Amer. Chem. J.*, 1906. **36**, 427) obtained the value $1{\cdot}0\times10^{-6}$ at 0°, our own result being 6×10^{-7} at 18° (using unplatinised electrodes †).

As regards the molecular conductivity of solutes at infinite dilution (λ_∞) in acetone, considerable vagueness exists. Carrara (*loc. cit.*) states that λ_∞ for triethylsulphine iodide is 167 (as determined by direct experiment). Walden (*Zeitsch. physikal. Chem.*, 1906, **54**, 222) found for tetraethylammonium iodide at 25°

* For a general account of the electrochemistry of non-aqueous solutions compare Carrara: "Elektrochemie der nichtwässrigen Lösungen," Ahrens' *Sammlung*, **12**; also Neustadt, *Diss.*, Breslau, 1909.

† These are preferable to platinised ones, as they eliminate the possibility of catalytic reactions when the solvent is an organic substance.

$\lambda_x = 225$. Dutoit and Levier (*loc. cit.*) give the following values for some simple salts at 18°:

	Li.	Na.	K.	NH_4.
Br	155	158	155·5	157·5
I	157	155	157·5	157·5
CNS	—	169	170·0	171·0
NO_3*	132	—	—	—

* Benz, *Diss.*, Lausanne, 1905.

From these results Dutoit and Levier conclude that Kohlrausch's law of the independent migration of the ions is valid for solutions in acetone. The same authors have applied Ostwald's dilution law to some of the above salts, but find that the "constant" falls with increasing dilution.

In connexion with the question of transport numbers, Carrara (*loc. cit.*) draws the conclusion that in general there is a tendency on the part of each ion to reach a limiting value independent of the nature of the solvent. This scarcely seems to be borne out in the case of acetone, however. In the particular instance of silver nitrate, Jones and Rouiller (*loc. cit.*) state that the solubility of the salt in acetone is too slight to make a direct determination of the transport number, but that a value may be obtained by extrapolation from results obtained in acetone–water mixtures, the acetone concentration rising from zero to 75 per cent. Naturally, the extrapolation is a rather large one, and Jones and Rouiller have only felt justified in giving the result as an inequality, namely, the transport number of NO_3' at 25° in acetone $>0·62$.

Experiments with methyl alcohol–acetone mixtures also lead on extrapolation to a value for the transport number greater than 0·6.

Experimental.

Kahlbaum's acetone was twice distilled over metallic calcium, the middle fraction being kept in a glass bottle, from which moisture was carefully excluded by calcium chloride tubes.

The most concentrated solution of silver nitrate conveniently prepared was 0·02*N*. The solvent and solutions were kept, and the measurements carried out in weak artificial light, as it was noticed that on exposure to sunlight a brown precipitate forms in the solutions. Under the conditions specified the solutions remain permanently homogeneous.

I.—*Conductivity Measurements.*

The usual Wheatstone bridge and telephone method was employed. The cell, from which moisture was excluded, contained

two large unplatinised platinum plates close together, the ce[illegible] constant being small, namely, 0·09213.

The measurements were made at 18°, an oil-bath being employed as the resistances were in all cases fairly large. The following table contains the specific and molecular conductivities of silver nitrate

TABLE I.

Concentration in gram-mols./litre.	Specific conductivity (mhos) × 10^5.	λ_v. Molecular conductivity
0·02	14·37	7·19
0·01	10·17	10·17
0·007	7·42	10·60
0·005	5·50	11·00
0·0035	3·97	11·34
0·002	2·51	12·54
0·001	1·46	14·62
0·0005	0·98	19·68

Our values at 18° are slightly lower than those of Laszczynski and slightly higher than those of Jones and Rouiller (at 25°).

The value of λ_∞ for silver nitrate cannot be obtained directly. The empirical expression $\lambda_\infty \eta$ = constant (compare Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 207) independent of the solvent, η being the viscosity of the solvent, does not appear to hold for acetone; thus, on comparing the viscosities of water and acetone, one finds that λ_∞ for silver nitrate in acetone = 371, a value which is certainly too great. Again, Kohlrausch's expression, $\lambda_v = \lambda_\infty - a\sqrt[3]{c}$, where a is a constant and c the concentration, has found application in those cases in which λ_v is a linear function of $\sqrt[3]{c}$; although this condition is approximately fulfilled in the present instance, the values for λ_∞ given by the formula vary from 45 to 78.

A moderate approximation may, however, be obtained in the following way: According to Laszczynski, λ_∞ for simple salts in acetone is 1·3 times that in water. For silver nitrate at 18° λ_∞ = 116, and hence in acetone λ_∞ = 151. This is not very different from the directly determined values for alkali bromides and iodides in acetone (λ_∞ = 155—160, Dutoit and Levier), and since in water the λ_∞ for silver nitrate does not differ much from that of these salts, we have assumed that the same holds for acetone solutions and have taken λ_∞ for silver nitrate = 150. The conclusions which we draw from the results in which λ_∞ is employed are not invalidated, even if a large percentage error (up to 30 per cent.) were involved in this quantity; further, the majority of the electromotive force measurements given later are independent of λ_∞.

The following table contains the degrees of dissociation of silver nitrate in acetone, the Ostwald dilution law $\alpha^2/(1-\alpha)v$, and the

empirical expressions $\alpha^3/(1-\alpha)^2v$ and $\alpha^2/(1-\alpha)\sqrt{v}$ of van't Hoff and Rudolphi respectively.

TABLE II.

Molar concentration.	$\alpha=\lambda_v/\lambda_\infty$.	Ostwald K.	van't Hoff K.	Rudolphi K.
0·02	0·048	$0·0_448$	$0·0_5244$	$0·0_3342$
0·01	0·068	50	362	496
0·007	0·070	37	277	442
0·005	0·073	29	226	407
0·0035	0·075	21	173	360
0·002	0·084	15	141	345
0·001	0·097	14	102	329
0·0005	0·131	09	149	441

The Ostwald constant falls steadily as the dilution increases. The van't Hoff constant is also not very satisfactory, the most consistent values being given by Rudolphi's formula. It is thus apparent that silver nitrate in acetone behaves like a strong electrolyte in not obeying Ostwald's law, but at the same time the extent of the dissociation is that of a weak electrolyte (in water). This opens the question as to what is the criterion to be employed to decide whether an electrolyte is "weak" or "strong."

The conductivity of lithium nitrate in acetone (which is required in connexion with the *E.M.F.* measurements) was also determined, with the following result.

TABLE III.

Lithium Nitrate in Acetone at 18°.

Molar concentration.	Specific conc. $\times 10^3$.	λ_v	$\alpha=\lambda_v/\lambda_\infty$.	Ostwald K.	Rudolphi K.
0·343*	2·4	7·0	0·053	$0·0_2101$	$0·0_2176$
0·1715	1·39	8·1	0·061	067	160
0·0858	0·82	9·54	0·072	048	—
0·0429	0·50	11·6	0·088	036	—
0·0214	0·31	14·5	0·110	029	$0·0_2200$
0·0107	0·20	19·0	0·144	026	—
0·0053	0·13	24·5	0·186	022	—
0·0026	0·087	33·4	0·253	022	$0·0_2430$
0·0013	0·057	44·0	0·333	022	—
0·00065	0·037	57·0	0·432	021	$0·0_2840$
0·00032	0·024	75·0	0·568	023	0·0120

* Saturated.

The value of λ_∞ for lithium nitrate as determined by Benz (Dutoit and Levier, *loc. cit.*) is 132, and this has been employed in the calculation of the three last columns in the above table.* It will be observed that for dilutions $v>100$ the Ostwald expression is constant, whilst the Rudolphi formula does not hold—and this

* Kohlrausch's formula is also inapplicable here, because λ is not a linear function of

in spite of the fact that the dissociation is much greater than is the case of silver nitrate. Dissociation of itself is therefore not necessarily the source of the inapplicability of the Ostwald law. From the data given above it is found that the concentration of NO_3' in the saturated solution of lithium nitrate is 0·0182 gram-ion per litre at 18°. This quantity is required later.

II.—*Electromotive Force Measurements.*

A calibrated slide-wire potentiometer (Land- und Seekabelwerke) accurate to 0·1 millivolt was employed. The Weston cell was taken as standard ($E.M.F. = 1{\cdot}0183$ volts). Since it was anticipated that the quantity of current which could be obtained from the silver nitrate concentration cells would be very small, a galvanometer was not employed. Instead, an evacuated capillary electrometer was used. This type of instrument suffers as a rule from the defect that its capacity is too great. The vacuum type, however, is much more sensitive than the ordinary form, probably due to the fact that since air is excluded the quantity of Hg^{++} ions in solution is less than in the ordinary instrument, and hence the capacity of the Helmholtz double-layers is less.* Employing the Weston cell as a source of *E.M.F.*, it was observed that with the electrometer readings could be made to 0·1 millivolt. With the silver nitrate acetone cells the reading is only accurate to 2 millivolts. The sensitivity is therefore not sufficient for very accurate work.

Electromotive Forces which include Liquid/Liquid Potential Difference.

For the ordinary type of cell,

$$\mathrm{Ag} \left| \underset{c_1.}{\mathrm{AgNO_3}} \right\vdots \underset{c_2.}{\mathrm{AgNO_3}} \left| \mathrm{Ag}, \right.$$

the expression for the electromotive force at 18° is:

$$E = \frac{2v}{u+v}\,\frac{RT}{nF}\log\frac{a_1c_1}{a_2c_2} \text{ or } \frac{2v}{u+v}\;0{\cdot}0577\log\frac{\lambda_1c_1}{\lambda_2c_2},$$

where λ_1, λ_2 are the molecular conductivities at the $AgNO_3$ concentrations c_1 and c_2; $v/u+v$ = transport number of $NO_3' = 0{\cdot}62$.

It was our object to investigate if the Nernst formula held good for acetone solutions. Table IV contains the results obtained, the headings of the columns being self-explanatory.

It will be observed that the differences between observed and calculated values are about as frequently positive as negative. The results obtained therefore support the view that Nernst's formula is applicable. Incidentally, also, the agreement obtained goes to show

* Experiments are being undertaken in this laboratory with a view further to improve, if possible, the sensitivity of the capillary electrometer.

TABLE IV.

Temperature.	Molar concentration of $AgNO_3$. c_1.	c_2.	E.M.F. observed 1st determination.	2nd.	3rd.	E.M.F. calculated.
19°	0·02	: 0·01	0·014	0·013	{0·015, 0·013}	0·011
19·5	0·02	: 0·007		0·020	0·020	0·028
19	0·02	: 0·005	[0·029]	0·034	0·035	0·033
20	0·02	: 0·0035		0·045	0·045	0·040
19	0·02	: 0·002	0·054	0·052	0·052	0·054
19	0·02	: 0·001	0·056	0·057	0·058	0·070
19	0·02	: 0·0005	{0·085, 0·086}	0·084	0·085	0·087
20	0·02	: 0·00005		0·121	0·121	—
19	0·01	: 0·007		0·012	0·011	0·009
19	0·01	: 0·005		0·025	0·024	0·019
20	0·01	: 0·0035		0·029	{0·028, 0·027}	0·026
19	0·01	: 0·002		0·037	0·038	0·043
19	0·01	: 0·001		0·045	0·045	0·060
19	0·01	: 0·0005		0·074	0·073	0·073
19	0·01	: 0·00005	0·119	0·120	0·118	—
20	0·007	: 0·005		0·013	0·015	0·009
20	0·007	: 0·0035		0·015	{0·017 *, 0·016}	0·019
20	0·007	: 0·002		0·032	0·032	0·033
20	0·007	: 0·001		0·042	0·042	0·050
20	0·007	: 0·0005		{0·055, 0·056}		0·062

* Neustadt measured this combination, his value being 0·016—0·017v, which is in good agreement with our result. Neustadt did not attempt to calculate the *E.M.F.*

that the value 0·62 for the transport number of NO_3' in acetone must be fairly correct. Employing this, we can calculate the magnitude of the liquid/liquid potential differences (included in the above measurements) by means of the expression:

$$E_1 = \frac{u-v}{u+v} \, 0{\cdot}0577 \log \frac{\lambda_1 c_1}{\lambda_2 c_2}.$$

TABLE V.

Liquid/Liquid Potential Difference in Volts (*at* 18°).

Molar concentration of $AgNO_3$.	P.D. calculated.
0·02 : 0·01	0·002
0·02 : 0·001	0·013
0·01 : 0·007	0·001
0·01 : 0·005	0·004
0·01 : 0·002	0·008
0·01 : 0·001	0·012
0·01 : 0·0005	0·014

The liquid/liquid potential difference is therefore not negligible when the concentration-ratio of the salt exceeds 5.

Attempts to Eliminate the Liquid/Liquid Potential Difference.

As ammonium nitrate has been frequently employed in aqueous solution to eliminate the liquid potential difference, we had hoped to employ it in the present case, but its solubility in acetone is very slight, as is also the solubility of sodium nitrate. Ammonium acetate dissolves to a certain extent, but it is unsuitable for the purpose, since the solution (in presence of air) darkens, and on pouring it into water a green fluorescence is observed, indicating the formation of a compound. The solubility of potassium nitrate in acetone at 18° was found to be 0·001 gram-molecule per litre. A saturated solution of dry lithium nitrate was under the same conditions found to be 0·343*N*. Owing to its greater solubility, lithium nitrate was therefore employed, although the great inequality in the mobility of its ions in water is not a recommendation.* Two sets of experiments were carried out, (*a*) with lithium nitrate (or potassium nitrate) interposed between the silver nitrate solutions, and (*b*) with lithium nitrate present throughout the cell.

(a) Potassium and Lithium Nitrates Interposed.

The following table contains the *E.M.F.* values obtained with potassium nitrate as the middle liquid:

TABLE VI.

Temperature.	Molar concentration of $AgNO_3$. c_1. : c_2.	*E.M.F* observed.	*E.M.F.* observed without KNO_3 interposed.
19°	0·01 : 0·007	0·011	0·011
19	0·01 : 0·005	0·024	0·024
20	0·01 : 0·0035	0·028	0·028
19	0·01 : 0·002	0·048	0·037
19	0·02 : 0·007	0·020	0·020
19	0·02 : 0·005	0·031	0·035
20	0·02 : 0·0035	0·045	0·045
19	0·02 : 0·002	0·053	0·052
19	0·02 : 0·001	0·058	0·058

The interposition of potassium nitrate has no reasonable effect, as was to be expected from its slight solubility. The measurements in this case were the most difficult to obtain.

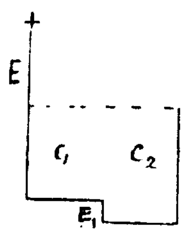
The following table contains the results obtained on interposing saturated lithium nitrate solution (0·343*N*) as the middle liquid:

* This is probably of little significance, however, since the Li ion has been shown to be greatly hydrated in aqueous solution, while it may be "normal" in acetone.

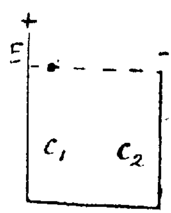
TABLE VII.

Temperature.	Molar concentration of $AgNO_3$. c_1 : c_2.	*E.M.F.* observed.	*Increase* in *E.M.F.* in volts due to interposition of $LiNO_3$.
19°	0·02 : 0·01	0·019, 0·020	0·005
19	0·02 : 0·007	0·028	8
19	0·02 : 0·005	0·041	7
19	0·02 : 0·0035	0·052	7
19	0·02 : 0·002	0·068	16
19	0·02 : 0·001	0·065	7
19	0·02 : 0·0005	0·134 (!)	47 (!)
19	0·01 : 0·007	0·017, 0·019	6
19	0·01 : 0·005	0·034	9
19	0·01 : 0·0035	0·035	8
20	0·01 : 0·002	0·064	7
19	0·01 : 0·001	0·053	8
20	0·01 : 0·0005	0·075	2
20	0·007 : 0·005	0·022	8
20	0·007 : 0·0035	0·023	7
20	0·007 : 0·002	0·038, 0·039	6
20	0·007 : 0·001	0·048	6
20	0·007 : 0·0005	0·063	7

The important fact brought out by the above results is that saturated solution of lithium nitrate *raises* the *E.M.F.* of the cell instead of lowering it, as one would expect in accordance with the following:



$c_1 > c_2$. Liquid/liquid P.D. $= E_1$.
Transport number of anion $> 0·5$.
Net *E.M.F.* of cell $= E$.



$E_1 = 0$.
Net E should be less than in previous case.

The lithium nitrate solution, instead of eliminating E_1, sets up a potential difference of its own in the same sense as the E_1 in the original case.

(*b*) *Lithium Nitrate Solution Throughout the Cell.*

In view of the abnormal behaviour of lithium nitrate when interposed, it is of interest to examine its effect when distributed throughout the cell, in which case, on theoretical grounds, any convenient electrolyte sufficiently soluble should eliminate the liquid/liquid potential difference. First, it is necessary to tabulate the

values for the silver ion concentration in the various solutions when allowance is made for the presence of the saturated lithium nitrate solution. As we have already seen, this solution gives rise to a NO_3' concentration 0·0182 gram-ions per litre, which may be regarded as remaining practically constant in all cases, thereby throwing back the dissociation of the silver nitrate to a different extent in each solution. The problem would be easy if silver nitrate in acetone obeyed the dilution law, but this is not the case. As an approximation, however, the silver ion concentration in presence of the lithium salt has been calculated, first, by employing the various values found for the Ostwald "constant" at the corresponding molar concentrations of the silver salt, the results being given in the following table, column 2; and, secondly, by employing the mean of the values of the Ostwald constant, the results in this case being given in the third column.

TABLE VIII.

Molar concentration of $AgNO_3$.	$[Ag^{\cdot}]$ calculated from the corresponding "K."	$[Ag^{\cdot}]$ calculated from the mean $K = 0·0_4 25$.
0·02	$0·0_4527$	$0·0_4307$
0·01	$0·0_4275$	$0·0_4154$
0·007	$0·0_4142$	$0·0_4107$
0·005	$0·0_579$	$0·0_577$
0·002	$0·0_516$	$0·0_538$
0·001	$0·0_677$	$0·0_515$
0·0005	$0·0_625$	$0·0_677$

The values of the silver ion concentration thus obtained are used to calculate the *E.M.F.* of the cell (containing lithium nitrate throughout), the formula when there is no liquid/liquid potential difference being:

$$E = 0·0577 \log \frac{[Ag^{\cdot}]_{I}}{[Ag^{\cdot}]_{II}},$$

in which the square brackets denote concentration terms. In the following table are given the observed *E.M.F.*'s, the *E.M.F.* calculated from the data in column 2, table VIII, and the *E.M.F.*'s calculated from column 3, table VIII, respectively.

TABLE IX.

Temperature 19°.

Molar concentrations of $AgNO_3$.	*E.M.F.* in volts observed.	*E.M.F.* calculated from col. 2, table VIII.	*E.M.F.* calculated from col. 3, table VIII.
0·02 : 0·01	0·013	0·0163	0·0173
0·01 : 0·007	0·0122	0·0166	0·009
0·01 : 0·005	0·0245, 0·0249	0·0313	0·0173
0·01 : 0·002	0·060	0·0715	0·035
0·01 : 0·001	0·069	0·0895	0·0583
0·01 ; 0·0005	0·086	0·118	0·0759

It may be noted that with lithium nitrate throughout the cell measurements could be made much more easily than in the previous cases. The error does not exceed 0·5 millivolt.

We may also obtain a series of values by calculation, without taking the silver ion concentration values into account, if we assume that the dissociation of silver nitrate approximately obeys the dilution law, and that the dissociation is small compared to that of lithium nitrate. In such a case we have:

$$\frac{[Ag^{\cdot}]_{I}}{[Ag^{\cdot}]_{II}} = \frac{\text{Molar concentration } AgNO_{3I}}{\text{Molar concentration } AgNO_{3II}}.$$

The values worked out by this method were practically identical with those given in column 4, table IX.

It will be observed that the found values lie between the two series of calculated values. It is therefore impossible to state with certainty whether there is agreement or not, the indefiniteness arising from the fact that silver nitrate does not obey Ostwald's dilution law accurately.

Summary.

(1) Silver nitrate in acetone is only slightly dissociated. It does not, however, obey Ostwald's dilution law, but gives a good constant in Rudolphi's expression.

(2) Lithium nitrate in acetone is much more dissociated than silver nitrate. For dilutions $v > 100$ Ostwald's law holds well. Rudolphi's expression does not hold.

(3) It has been shown that the electromotive force of the silver nitrate concentration cell in acetone at 19°, arranged so as to contain a liquid/liquid potential difference as well as electrode potential differences, is in quantitative agreement with Nernst's formula, the value of the transport number of NO_3' being taken as ·62.

(4) The interposition of a saturated solution of lithium nitrate between the two silver nitrate solutions, instead of eliminating the liquid/liquid potential difference, increases the latter by several millivolts. The introduction of lithium nitrate throughout the cell has the desired effect so far as it has been possible to decide in view of the approximate nature of our knowledge of the silver ion concentration.

In conclusion, we wish to thank Dr. N. T. M. Wilsmore for the interest which he has taken in these experiments.

PHYSICAL CHEMISTRY LABORATORY,
UNIVERSITY COLLEGE, LONDON.

CCXLII.—*Chemical Examination of Calabar Beans.*

By ARTHUR HENRY SALWAY.

THE so-called Calabar beans, the ripe seed of *Physostigma venenosum*, Balfour, have previously been the subject of several investigations, and their most important constituent—the alkaloid physostigmine or eserine—has long been recognised by most of the national Pharmacopœias on account of its valuable medicinal properties.

The first chemical examination of Calabar beans was conducted by Jobst and Hesse (*Annalen*, 1864, **129**, 115), who ascertained that their poisonous action is due to an alkaloid, which they designated physostigmine. This substance was obtained by them only as an amorphous, varnish-like mass, but a year later Vée (*Jahresber.*, 1865, 456) succeeded in isolating the alkaloid in a crystalline state. The last-mentioned investigator found that the alkaloid melted at 69°, and proposed for the crystalline base the name eserine. Jobst and Hesse, in a later investigation (*Annalen*, 1867, **141**, 913) assigned to physostigmine the formula $C_{15}H_{21}O_2N_3$, but still expressed doubt regarding its crystalline character, although it is now known that under suitable conditions the alkaloid, as stated by Vée (*loc. cit.*), can be obtained in the crystalline form.

In the year 1876 Harnack and Witkowski (*Arch. experim. Path.* 1876, 401) indicated the presence of a second alkaloid in Calabar beans, for which they proposed the name calabarine. This substance was very indefinite in character, being chiefly distinguished by its tetanus-like effects on the living organism. Subsequent investigations, notably that of Ehrenberg (*Verh. Ges. Deut. Naturf. Aerzte* 1893, II, 102), have shown that calabarine was in all probability a product of decomposition, and could not have pre-existed in the Calabar bean. It is evident, however, that besides physostigmine a very small proportion of other alkaloids is contained in the Calabar bean; thus, in the year 1888, a crystalline base, differing from physostigmine, was obtained by Böhringer & Söhne (*Pharm. Post*, 1888, **21**, 663), and termed by them eseridine. This base was stated to melt at 132°, to be much less poisonous than physostigmine, and on heating with dilute mineral acids to become converted into the latter alkaloid. Eseridine has been further examined by Eber (*Pharm. Zeit.*, 1892, **37**, 483), who assigned to it the formula $C_{15}H_{23}O_3N_3$, and it is thus seen to differ from physostigmine only in the elements of one molecule of water.

Ehrenberg (*loc. cit.*) succeeded in isolating a third alkaloid from the Calabar bean. This substance, which is present in extremely

small proportions, was named eseramine, and the empirical formula $C_{16}H_{25}O_3N_4$ assigned to it. It was described as a substance very sparingly soluble in ether and melting at 238—240°. Still another alkaloid of Calabar bean has more recently been described by Ogui (*Apoth. Zeit.*, 1904, **19**, 891). This base is stated to be isomeric with physostigmine, and therefore designated *iso*physostigmine. The only information concerning it appears to be the fact that it is insoluble in ether, and yields a sulphate melting at 200—202°.

Little is known regarding the constitution of physostigmine, and practically nothing of the alkaloids associated with it. It therefore seemed desirable to undertake some experiments for the purpose of throwing further light on the chemical constitution of these bases. To achieve this object a large quantity of Calabar beans was obtained and worked up for the isolation of the alkaloids. At the same time, the opportunity was taken to examine more completely the other constituents of the bean. The experiments undertaken in order to elucidate the constitution of physostigmine are reserved for a future communication.

EXPERIMENTAL.

A representative sample of the Calabar beans employed in this investigation, when assayed by the method of the United States Pharmacopœia, yielded 0·091 per cent. of alkaloid. The method referred to, however, was found to give results which were much too low, since the amount of physostigmine isolated when working on the large scale, as described below, was equivalent to 0·179 per cent. of the material employed. The low result by the above method of assay has been ascertained to be due to the fact that three extractions with ether (as required by the Pharmacopœia) are quite insufficient to remove the alkaloid completely from a solution which has been rendered alkaline with sodium hydrogen carbonate.

With the object of testing for the presence of an enzyme, 500 grams of powdered material were mixed with water and kept at the ordinary temperature for forty-eight hours. The liquid was then separated from the mass by filtration under pressure, and alcohol added to the filtrate. A caseous, white precipitate was thus produced, which was collected and dried in a vacuum desiccator over sulphuric acid, when it amounted to 14·5 grams. This substance, which gave the biuret reaction, slowly hydrolysed amygdalin, thus indicating the presence of an enzyme.

A further portion (50 grams) of the powdered bean was successively extracted in a Soxhlet apparatus with various solvents, when

the following amounts of extract, dried at 100°, were obtained:

Petroleum (b. p. 35—50°) extracted	0·38	grams	=	0·76	per cent.
Ether ,,	0·08	,,	=	0·16	,,
Chloroform ,,	0·18	,,	=	0·36	,,
Ethyl acetate ,,	0·13	,,	=	0·26	,,
Alcohol ,,	2·32	,,	=	4·64	,,
Total.........	3·09	,,		6·18	,,

For the purpose of a complete examination of the constituents of the bean 122·7 kilograms of finely powdered material were extracted by continuous percolation with hot alcohol. After removal of the greater part of the alcohol there remained a reddish-brown extract, amounting to 10½ kilograms. This extract, in convenient portions, was mixed with water, and the mixture distilled in a current of steam. The distillate, which contained a very small quantity of essential oil, was extracted with ether, the ethereal solution being washed, dried, and the ether removed. A pale yellow oil possessing a garlic-like odour and amounting to 1·5 grams was obtained.

After the above operation there remained in the steam distillation flask a large quantity of fatty oil floating on the surface of a reddish-brown aqueous liquid, which contained a brown, resinous powder in suspension. The fatty oil was separated, washed well with water, and set aside for subsequent examination, whilst the brown resin was collected and washed with water, the washings being added to the main portion of the aqueous liquid.

Isolation of Physostigmine, $C_{15}H_{21}O_2N_3$.

A small portion of the aqueous liquid was, in the first place, extracted successively with ether and amyl alcohol, but these solvents removed only small quantities of gummy material. The whole of the aqueous liquid was then rendered alkaline with an excess of sodium carbonate, and repeatedly extracted with ether until no further alkaloidal substance was removed by this treatment. The ethereal extracts were united, concentrated to a convenient volume, and then carefully shaken with successive portions of 5 per cent. sulphuric acid until the extract became just acid in reaction. The neutral solution of the sulphate of the alkaloid was then treated with an excess of a saturated solution of sodium salicylate, when the salicylate of the alkaloid was precipitated as an almost colourless, crystalline powder. This was collected, washed well with water, and dried in a vacuum desiccator over sulphuric acid. A further quantity of the salicylate of the alkaloid was obtained from the filtrate by rendering it alkaline with sodium carbonate, extract-

ing with ether, and subjecting the ethereal solution to the same process as that described above. The total crude salicylate thus obtained amounted to 330 grams, representing 219·7 grams of physostigmine, which is equivalent to 0·179 per cent. of the material employed in the investigation. In order to ascertain whether this crude salicylate was homogeneous or not, a considerable portion of the compound was subjected to systematic fractional crystallisation from alcohol. The fractions were found to be uniform in character, crystallising in stout, colourless prisms, melting at 180—181°, and were therefore homogeneous. (Found, C=64·1; H=6·6; N=10·2. Calc., C=63·9; H=6·5; N=10·2 per cent.)

It is evident that the above compound consisted of physostigmine salicylate. The free base was obtained from the latter by agitation with aqueous sodium carbonate in the presence of ether. The ethereal solution of physostigmine thus obtained was dried, and the solvent removed. The pale brown, viscid residue was dissolved in benzene, and the solution allowed to evaporate slowly at the ordinary temperature in a vacuum desiccator over sulphuric acid. After some time there was deposited a mass of crystals, which was collected and recrystallised several times from a mixture of benzene and petroleum. The physostigmine separated from this solvent in stout prisms, which melted at 86—87°. (Found, C=65·1; H=7·9. Calc., C=65·5; H=7·6 per cent.)

0·2659, made up to 20 c.c. with chloroform, gave α_D $-2°1'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-75·8°$.

The above specimen of physostigmine does not agree in melting point with the physostigmine obtained by Pictet and Polonowsky (*Bull. Soc., chim.*, 1893, [iii], **9**, 1008), who state that the alkaloid melts at 105—106°. A commercial sample of physostigmine was therefore procured, and this also melted at 105—106°. It was then found that the alkaloid is dimorphous, since the modification melting at 86—87° could be readily converted into the substance melting at 105—106° by recrystallisation in the presence of a crystal of the latter. The optical rotation of the compound melting at 105—106° was determined, and found to be identical with that of the modification melting at 86—87°, as recorded above:

0·3062, made up to 20 c.c. with chloroform, gave α_D $-2°19'$ in a 2-dcm. tube, whence $[\alpha]_D$ $-75·8°$.

Pictet and Polonowsky (*loc. cit.*) ascribe to physostigmine an optical rotation, $[\alpha]_D$ $-82°$, which is somewhat higher than the results obtained above.

Physostigmine does not yield any definite aurichloride or platinochloride, but a well-defined *picrate* was obtained, which crystallises

from dilute alcohol in feathery, yellow needles, melting at 114°. It is only sparingly soluble in hot water, but readily so in alcohol.

Isolation of Eseramine.

The ethereal liquid which had been shaken with dilute sulphuric acid for the separation of the physostigmine as above described was washed with water, dried, and the solvent removed. A small amount (about 2 grams) of a viscid, brown residue was thus obtained, which gradually became solid. Since the solid was not completely soluble in ether, it was digested with a small quantity of the latter, the sparingly soluble portion collected, and then purified by crystallisation from alcohol, when it separated in small, colourless needles, melting and decomposing at 245°. This substance was very sparingly soluble in ether, chloroform, or benzene, but readily so in hot alcohol. It dissolved in strong mineral acids, and yielded a precipitate with Mayer's reagent. It appears from the above properties that the substance is identical with the eseramine of Ehrenberg (*loc. cit.*), but the amount isolated (0·1 gram) did not admit of further examination.

Isolation of a New Alkaloid, Physovenine, $C_{14}H_{18}O_3N_2$.

The ethereal liquid from which the above-mentioned eseramine had been removed, yielded on evaporation a brown, oily residue which slowly crystallised. The crystals were separated from a little adhering oil, and then crystallised, first from dilute alcohol, and finally from a mixture of benzene and light petroleum. The substance separated from the latter solvent in small, colourless prisms, melting at 123°. The yield of pure substance amounted to 0·6 gram:

0·1024 gave 0·2395 CO_2 and 0·0669 H_2O. C = 63·8; H = 7·3.
0·1165 „ 0·2726 CO_2 „ 0·0736 H_2O. C = 63·8; H = 7·0.
0·1817 „ 17·2 c.c. N_2 (moist) at 25° and 764 mm. N = 10·6.
$C_{14}H_{18}O_3N_2$ requires C = 64·1; H = 6·9; N = 10·7 per cent.

The above-described alkaloid is not identical with any of the bases previously isolated from Calabar beans, and since no compound of the formula $C_{14}H_{18}O_3N_2$ appears to have been hitherto described, it is proposed to designate the new alkaloid, *physovenine*.

Physovenine, $C_{14}H_{18}O_3N_2$, is very soluble in alcohol, benzene, or chloroform, moderately so in ether, but insoluble in light petroleum or water. It is only a weak base, dissolving in concentrated mineral acids, but being reprecipitated on the addition of water. When physovenine is treated with barium hydroxide, there is an immediate precipitation of barium carbonate, and the solution rapidly

assumes a deep red colour. This behaviour of physovenine is very similar to that of physostigmine, since the latter under the influence of alkalis (Ehrenberg, *loc. cit.*) loses carbon dioxide and methylamine, and becomes converted successively into eseroline and a red colouring matter, rubreserine. It appears probable from the properties and composition of physovenine that the latter is an intermediate product in the conversion of physostigmine into eseroline, as represented by the following equations:

$$\underset{\text{Physostigmine.}}{C_{15}H_{21}O_2N_3} + H_2O = \underset{\text{Physovenine.}}{C_{14}H_{18}O_3N_2} + CH_3{\cdot}NH_2.$$

$$C_{14}H_{18}O_3N_2 = \underset{\text{Eseroline.}}{C_{13}H_{18}ON_2} + CO_2.$$

Physovenine is, like physostigmine, very powerfully myotic; thus a single drop of a 0·1 per cent. solution of the alkaloid in dilute alcohol when introduced into the eye produced after an interval of a few minutes a powerful contraction of the pupil, which attained its maximum effect half an hour after the injection.

A portion of the aqueous liquid from which the alkaloids had been extracted as described above, was rendered slightly acid with acetic acid, and then concentrated to a small bulk. A large amount of a viscid syrup was thus obtained, which readily reduced Fehling's solution. It was digested with hot alcohol, the alcoholic liquid decanted, and ethyl acetate added to the latter. In this manner a considerable quantity of a sugar was obtained, which yielded a glucosazone, melting and decomposing at 205°.

The Fatty Oil.

The fatty oil which had been isolated as previously described amounted to 1650 grams. Since it was found to contain a small quantity of alkaloidal substance of weakly basic character, it was extracted with 40 per cent. sulphuric acid. The acid extracts were rendered alkaline and extracted with ether. In this manner a small amount (1·5 grams) of a brown, viscid liquid was obtained, which partly solidified after keeping some time. On examination, the crystalline substance was found to be identical with the alkaloid physovenine, $C_{14}H_{18}O_3N_2$, previously isolated from the aqueous liquid.

A convenient portion (200 grams) of the fatty oil was next hydrolysed by heating with an excess of potassium hydroxide in the presence of alcohol, when a considerable quantity of ammoniacal vapours was evolved. After this treatment the greater part of the alcohol was removed, water added, and the alkaline liquid repeatedly

extracted with ether. The pale yellow ethereal extract was washed, dried, and the ether removed, when 10 grams of a crystalline residue were obtained. This was dissolved in hot alcohol, from which it separated in colourless leaflets, melting at 132—133°. The substance gave the colour reactions of the phytosterols, and evidently belonged to that class of compounds. Windaus and Hauth (*Ber.*, 1906, **39**, 4378; 1907, **40**, 3681) have already shown that the phytosterol of Calabar bean is a mixture of two compounds, namely, stigmasterol, $C_{30}H_{48}O$, and sitosterol, $C_{27}H_{46}O$, which were separated by them after conversion into the bromoacetyl derivatives. In order to ascertain whether the above crude phytosterol, melting at 132—133°, consisted of such a mixture, the substance was acetylated, and the acetyl derivative treated with bromine in the presence of acetic acid. The sparingly soluble bromo-derivative which separated was purified by crystallisation from a mixture of chloroform and alcohol, and was obtained in colourless leaflets, melting and decomposing at 205—[illegible] (Found, Br = 40·6. Calc., Br = 40·7 per cent.) This substance is evidently identical with the tetrabromoacetylstigmasterol described by Windaus and Hauth (*loc. cit.*). When debrominated by means of zinc dust the above compound yielded acetylstigmasterol (m. p. 140°), and the latter on hydrolysis was converted into stigmasterol, melting at 169°.

The mother liquors from the bromination, treated in the same manner, yielded successively acetylsitosterol (m. p. 128°) and sitosterol, $C_{27}H_{46}O$, melting at 134—135°. (Found, C = 83·7; H = [illegible]. Calc., C = 83·9; H = 11·9 per cent.) It is thus evident that the above crude phytosterol, melting at 132—133°, consists of a mixture of stigmasterol and sitosterol.

Isolation of Trifolianol, $C_{21}H_{34}O_2(OH)_2$.

The alkaline aqueous liquid from which the above-described crude phytosterol had been extracted by ether was acidified with dilute sulphuric acid, when a dark-coloured, semi-solid precipitate of fatty acids was produced. A portion of the precipitate was observed to be sparingly soluble in ether, and this was therefore separately collected, when it formed a dark-coloured solid amounting to [illegible] grams. This sparingly soluble substance was first digested with hot alcohol, which removed the greater part of the colouring matter, and then treated with boiling chloroform. The latter solvent extracted a small amount of a colourless solid, which was purified by crystallisation from dilute pyridine, when it separated in microscopic needles, melting and decomposing at 295°. When dissolved in chloroform and acetic anhydride and a drop of concentrated sulphuric acid

lded, it gave a transient pink coloration, changing to blue, and en to green. (Found, C = 71·4; H = 10·2. Calc., C = 71·6; H = 10·2 r cent.)

The properties of the above compound, together with the result its analysis, indicate that the substance is identical with trifoliol, $C_{21}H_{34}O_2(OH)_2$, which was first isolated from red clover flowers 'ower and Salway, Trans., 1910, **97**, 249). Its identity was nfirmed by the formation of diacetyltrifolianol, which crystallised flat, colourless needles, melting at 165—166°. (Found, C = 68·9; = 9·2. Calc., C = 68·8; H = 9·2 per cent.):

0·2118, made up to 20 c.c. with chloroform, gave α_D −0°31′ in a 2-dcm. tube, whence $[\alpha]_D$ −24·4°.

Isolation of a New Dihydric Alcohol, Calabarol, $C_{23}H_{34}O_2(OH)_2$.

The sparingly soluble substance which had been digested with oroform for the removal of the trifolianol, as above described, crystallised from dilute pyridine, when it separated in minute stals, melting and decomposing at 290—300°. It was found, wever, that this substance still contained a considerable proporn of trifolianol. A separation was effected by converting the stance into its benzoyl derivative and subjecting the latter to stematic fractional crystallisation from a mixture of chloroform d alcohol. In this manner two benzoyl compounds were isolated, lting at 165—170° and 195—196° respectively. The former was nd on analysis to be *dibenzoyltrifolianol*:

0·1109 gave 0·3052 CO_2 and 0·0822 H_2O. C = 75·1; H = 8·2.

$C_{35}H_{44}O_6$ requires C = 75·0; H = 7·9 per cent.

The benzoyl derivative melting at 195—196° was analysed with e following results:

0·1173 gave 0·3268 CO_2 and 0·0810 H_2O. C = 76·0; H = 7·7.
0·1088 „ 0·3036 CO_2 „ 0·0768 H_2O. C = 76·1; H = 7·8.

$C_{37}H_{44}O_6$ requires C = 76·0; H = 7·5 per cent.

0·5294, made up to 20 c.c. with chloroform, gave α_D +0°52′ in a 2-dcm. tube, whence $[\alpha]_D$ +14·7°.

It would appear from the above analysis that the benzoyl mpound melting at 195—196° is derived from a dihydric alcohol, H_xO_4. In order to isolate this compound in a state of purity quantity of the original mixture of trifolianol and the new hol was heated with equal quantities of chloroform and alcohol, the undissolved substance collected. On repeating the process ral times a homogeneous compound was obtained, which melted 245°. This was recrystallised from dilute pyridine, when it rated in colourless, microscopic needles:

0·0504 gave 0·1351 CO_2 and 0·0460 H_2O. C=73·1; H=10·1.

$C_{23}H_{36}O_4$ requires C=73·4; H=9·6 per cent.

The above substance is thus seen to possess the formula $C_{23}H_{36}O_4$. As it is a new compound it is proposed to designate it *calabarol*, with reference to the source from which it has been obtained.

Calabarol is very sparingly soluble in the usual organic solvents, but dissolves readily in pyridine. When dissolved in acetic anhydride and chloroform and a drop of concentrated sulphuric acid added, a pink coloration is produced, which rapidly changes to blue and then to green. Calabarol yields a *dibenzoyl* derivative, $C_{23}H_{34}O_4(CO{\cdot}C_6H_5)_2$, which crystallises from a mixture of chloroform and alcohol in well-formed, colourless needles, melting at 195—196°. It is readily soluble in ethyl acetate or chloroform, but very sparingly so in alcohol.

The properties of calabarol indicate that it is closely allied to a number of dihydric alcohols, which have been isolated in these laboratories, and which fall into two groups possessing the general formulæ $C_nH_{2n-6}O_4$ and $C_nH_{2n-8}O_4$ respectively. Calabarol, however, appears to belong to a new series of dihydric alcohols, which may be represented by the general formula $C_nH_{2n-10}O_4$.

Examination of the Fatty Acids.

The ethereal solution of fatty acids from which trifolianol and calabarol had been removed as described above, was washed, dried, and the ether removed. The residue was dissolved in hot alcohol, when a substance separated, which, after several crystallisations from alcohol, melted at 74—76°:

0·3073 required, for neutralisation, 8·85 c.c. $N/10$-KOH. Neutralisation value=161·5.

$C_{22}H_{44}O_2$ requires neutralisation value=165·0.

It appears from this result that the substance is behenic acid (m. p. 80—82°), although the melting point is somewhat low for the latter compound. In order, therefore, to effect a further purification, the substance was esterified, and the ethyl ester thus produced then distilled under diminished pressure. The first portion of the distillate having been discarded, the remainder was hydrolysed, when it yielded a fatty acid, melting at 77·5°. (Found, C=77·[illegible]; H=13·0. Calc., C=77·7; H=12·9 per cent.):

0·1775 required for neutralisation 5·2 c.c. $N/10$-KOH. Neutralisation value=164·3.

$C_{22}H_{44}O_2$ requires neutralisation value=165·0.

The substance was thus definitely identified as behenic acid

The remaining portion of the fatty acids was converted into the lead salt, and the latter treated with ether in the usual manner for the separation of the saturated from the unsaturated acids. The portion of lead salt insoluble in ether was collected, and the fatty acids regenerated and crystallised from alcohol. The first crystalline deposits consisted of behenic acid, melting at 77°. The subsequent deposits melted at about 55—60°, and were evidently mixtures. In order to ascertain the constituents of this product, it was dissolved in alcohol and fractionally precipitated by the successive addition of small portions of a concentrated solution of barium acetate. In this manner four fractions were obtained, from each of which the fatty acid was regenerated, then crystallised once from alcohol, and titrated with $N/10$-potassium hydroxide. The neutralisation values of the several fractions were 202·5, 205·9, 207·0, and 209·5, whilst their melting points were 55°, 59°, 59°, and 60° respectively. These results indicated the presence of palmitic and stearic acids.

The unsaturated acids obtained from that portion of the lead salt which was soluble in ether amounted to 80 grams. When distilled under diminished pressure a yellow oil which passed over at ...–240°/15 mm. was obtained. An analysis and a determination of the constants led to the following results:

0·1064 gave 0·3004 CO_2 and 0·1128 H_2O. C = 77·0; H = 11·8.

Neutralisation value = 199·6; Iodine value = 139.

$C_{18}H_{34}O_2$ requires C = 76·6; H = 12·1 per cent. Neutralisation value = 198·9; Iodine value = 90·1.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent. Neutralisation value = 200·4; Iodine value = 181·4.

It is thus evident that the liquid acids consisted of a mixture of oleic and linolic acids.

Examination of the Resins.

The resin which had been separated from the aqueous liquid in the manner previously described, consisted for the most part of a brown powder, which was very sparingly soluble in the usual organic solvents. This product was mixed intimately with purified sawdust, the mixture dried, and then extracted in a Soxhlet apparatus successively with petroleum, ether, chloroform, ethyl acetate, and alcohol.

Petroleum Extract of the Resin.

This consisted of a brown, fatty oil, amounting to 65 grams. In order to ascertain whether the oil contained any alkaloid, it was dissolved in ether, and the ethereal solution shaken with dilute

sulphuric acid. The acid extracts yielded, however, only a very small quantity of a brown oil, which apparently consisted of physostigmine.

The ethereal solution which had been shaken with dilute sulphuric acid was washed, dried, and the solvent removed. The residue was then hydrolysed, and the products of hydrolysis examined in a manner similar to that previously described in connexion with the fatty oil of Calabar bean. The following constituents were found to be present: stigmasterol, sitosterol, trifolianol, calabarol, and behenic, palmitic, stearic, oleic, and linolic acids.

Ether, Chloroform, and Ethyl Acetate Extracts of the Resin.

These extracts were dark brown, gummy solids, amounting to 5, 17·5, and 11 grams respectively. They were separately examined, but nothing of a definite nature was isolated from them.

Alcoholic Extract of the Resin.

This was a dark brown syrup amounting to 41 grams. It was dissolved in alcohol, and the solution heated for some time with dilute sulphuric acid. After removal of the alcohol in a current of steam, there remained a black, resinous mass and a deeply coloured aqueous liquid. The former was collected and examined, but yielded nothing definite. Since a small portion of the aqueous liquid gave a precipitate with Mayer's reagent, the whole was rendered alkaline with sodium carbonate, and the alkaline mixture extracted repeatedly with ether. The ethereal extracts were united and agitated with small portions of dilute sulphuric acid until the liquid was just acid in reaction. The extracts thus obtained were treated with a concentrated solution of sodium salicylate, yielding 3 grams of a crystalline solid, which was found to be identical with physostigmine salicylate, melting at 180—181°.

The alkaloid isolated as above described could not have existed as such in the alcohol extract of the resin, but was evidently present in some form of combination.

Summary.

The results of this investigation have shown that the Calabar bean (*Physostigma venenosum*, Balfour) contains, in addition to some essential oil, resin, and other amorphous substances, the following compounds:

Physostigmine, $C_{15}H_{21}O_2N_3$.—This alkaloid was found to be dimorphous, since two interconvertible modifications were obtained, melting at 86—87° and 105—106° respectively. The amount of

alkaloid isolated was equivalent to 0·179 per cent. of the Calabar beans employed.

Physovenine, $C_{14}H_{18}O_3N_2$, a new alkaloid, melting at 123°. Like physostigmine, it produces a powerful myotic effect on the pupil of the eye.

Eseramine, an alkaloid melting at 245°.

Calabarol, $C_{23}H_{36}O_4$, a new dihydric alcohol (m. p. 245°), which yields a *dibenzoyl* derivative, melting at 195—196°.

Trifolianol, $C_{21}H_{36}O_4$, a dihydric alcohol previously isolated from red clover flowers.

Stigmasterol, $C_{30}H_{48}O$, and sitosterol, $C_{27}H_{46}O$.

Glycerides of behenic, stearic, palmitic, oleic, and linolic acids.

A sugar yielding *d*-phenylglucosazone (m. p. 205°).

In the course of the present investigation no evidence has been obtained of the presence in Calabar beans of the alkaloid designated by Ogui (*loc. cit.*) as "*iso*physostigmine," or of the "eseridine" of Boehringer & Söhne (*loc. cit.*).

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

CCXLIII.—*Contributions to the Chemistry of the Terpenes. Part XII. Synthesis of a Menthadiene from Thymol, and of a Diethyl*cyclo*hexadiene from Phenol.*

By GEORGE GERALD HENDERSON and ROBERT BOYD, B.Sc., Carnegie Research Scholar.

Preparation of a Menthadiene from Thymol.

THYMOMENTHOL (hexahydrothymol), $C_{10}H_{19}\cdot OH$, was first prepared synthetically by Brunel (*Compt. rend.*, 1905, **140**, 252) according to the method of Sabatier and Senderens, namely, by passing a mixture of thymol vapour and hydrogen through a tube containing finely divided nickel at a temperature of 160—170°. When heated with either potassium hydrogen sulphate or phosphoric oxide this thymomenthol yielded a menthene, $C_{10}H_{18}$, but as these dehydrating agents tend to bring about intramolecular rearrangements, the constitution of the hydrocarbon obtained by these methods remained uncertain. As we proposed to make use of this menthene for the preparation of a menthadiene, it appeared advisable to attempt to

dehydrate the thymomenthol by means of oxalic acid in order to obviate the risk of rearrangement. This reagent proved effective under suitable conditions.

A quantity of thymomenthol was prepared according to Brunel's method, and some of the product, which is a colourless liquid with a pleasant odour resembling that of mint, was boiled for a considerable time under a reflux condenser with an 8 per cent. aqueous solution of oxalic acid. The result was not satisfactory, little or no change taking place, and the use of stronger solutions led to no improvement. Finally, in order to effect dehydration, it was found necessary to heat the thymomenthol with anhydrous oxalic acid for several days. When the reaction appeared to be completed, the contents of the flask were distilled in a current of steam, with the result that a colourless, oily liquid passed over, whilst a smaller quantity of a non-volatile substance remained in the flask. The liquid distillate was separated from the condensed water, dried with potassium hydroxide, and fractionally distilled. The fraction which boiled at 166—170° was retained, and the portion of higher boiling point again heated with oxalic acid. Ultimately, after further fractionation, we obtained a quantity of a clear, colourless liquid with a pleasant odour, which had the following constants: boiling point 167—169° under atmospheric pressure, D_{20}^{20} 0·8188, n_D 1·45363. The physical properties of this menthene agree with those of Brunel's preparation, and it is therefore evident that when thymomenthol is dehydrated by means of oxalic acid the product is the same as that obtained by using either potassium hydrogen sulphate or phosphoric oxide.

According to its method of formation from thymomenthol (I.), the hydrocarbon must be either Δ^2- (II) or Δ^3-menthene (III). We found that it yields the characteristic crystalline nitrosochloride, melting at 133°, and is therefore the Δ^3-isomeride:

$$\begin{array}{ccc} \begin{array}{l} CH_2\text{-}CHMe\text{-}CH_2 \\ CH_2\cdot CHPr^\beta\ CH\cdot OH \end{array} & \begin{array}{l} CH_2\text{-}CHMe\text{-}CH \\ CH_2\cdot CHPr^\beta\cdot CH \end{array} & \begin{array}{l} CH_2\cdot CHMe\cdot CH_2 \\ CH_2\cdot CPr^\beta{=}CH \end{array} \\ \text{(I.)} & \text{(II.)} & \text{(III.)} \end{array}$$

The other substance obtained by heating thymomenthol with anhydrous oxalic acid, which did not volatilise with steam, was proved to be *thymomenthyl oxalate*, $C_2O_4(C_{10}H_{19})_2$, which is formed as an intermediate product. This ester was separated from the other contents of the distillation flask by means of ether, the ethereal solution washed and dried, and the ether removed. On distillation of the residue a clear, colourless liquid passed over, which solidified on keeping. After crystallisation from alcohol the ester was obtained in large, colourless, lustrous prisms, which melted at 90°. It is very readily soluble in ether, benzene, or chloroform.

fairly readily so in alcohol, light petroleum, or acetic acid, and insoluble in water. It is rapidly hydrolysed when heated with aqueous sodium hydroxide, yielding oxalic acid and *β-thymomenthol*, a crystalline solid melting at 29°:

0·2183 gave 0·5769 CO_2 and 0·2014 H_2O. C = 72·1; H = 10·3.
$C_{22}H_{38}O_4$ requires C = 72·1; H = 10·4 per cent.

From the Δ^3-menthene a menthadiene was prepared in the following manner: A solution of the hydrocarbon (1 mol.) in about four times its weight of glacial acetic acid was cooled with ice-water, and a cooled solution of bromine (1 mol.) in the same solvent slowly added. The product was poured into water, and the *menthene dibromide*, $C_{10}H_{18}Br_2$, which separated as a heavy, oily liquid, extracted with ether. The ethereal solution was washed and dried, the ether removed, and the residual liquid distilled under diminished pressure. The dibromide is a colourless, rather viscous liquid, which boils at 125–128°/30 mm. It is unstable, quickly becoming dark in colour.

The dibromide was heated for several hours on the water-bath under a reflux condenser with excess of alcoholic potassium hydroxide. When no further separation of potassium bromide was observed, the contents of the flask were distilled in a current of steam, and the oily liquid which passed over was separated from the condensed water by agitation with light petroleum. The solution was dried, the petroleum removed by distillation, and the residual liquid purified by repeated distillation over sodium.

The *menthadiene*, $C_{10}H_{16}$, obtained in this manner is a colourless liquid with a pleasant odour somewhat like that of limonene, and has the following constants: boiling point 173·5° under atmospheric pressure, D_{20}^{20} 0·8337, n_D 1·46539. It at once reduces potassium permanganate in the cold, and unites additively with bromine, but it does not form a stable tetrabromide at the ordinary temperature, for when more than two atomic proportions of bromine are added, evolution of hydrogen bromide begins. It does not appear to form a nitrosite under the usual conditions. On exposure to the air it absorbs oxygen fairly rapidly:

0·2555 gave 0·8206 CO_2 and 0·2797 H_2O. C = 87·7; H = 12·1.
0·1876 „ 0·6064 CO_2 „ 0·2070 H_2O. C = 88·1; H = 12·2.
$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

Since Δ^3-menthene dibromide has the formula

$$\begin{array}{l}CH_2\cdot CHMe-CH_2\\ |\qquad\qquad\quad\ |\\ CH_2\cdot CBrPr^{\beta}\cdot CHBr\end{array}$$

probably the menthadiene prepared from it by elimination of two

molecules of hydrogen bromide in the manner described above is the $\Delta^{2:4}$-isomeride, with the formula: $\begin{matrix} CH_2\cdot CHMe\cdot CH \\ CH = CPr^{\beta}\cdot CH \end{matrix}$.

From menthol, through menthyl chloride, Birkenheim (*Ber.*, 1892, **25**, 690) prepared a hydrocarbon, $C_{10}H_{18}$, with the following constants: boiling point 170°, D_{20}^{20} 0·8160, n_D 1·4536. By addition of bromine to this compound and subsequent elimination of hydrogen bromide, he obtained a hydrocarbon, $C_{10}H_{16}$, which boiled at 172—174° and had D_{20}^{20} 0·8408. There can be little doubt that the menthene and menthadiene which we prepared synthetically from thymol are identical with the corresponding hydrocarbons which Birkenheim obtained directly from menthol.

Preparation of 1:3-*Diethyl*cyclo*hexadiene from Phenol.*

Considering that it would be of interest to compare the properties of the terpenes with those of isomeric hydrocarbons of the formula $C_{10}H_{16}$, we proceeded, in the first instance, to prepare a diethylcyclohexadiene from phenol in the following manner:

A quantity of 3:5-diethylphenol was prepared by condensing phenol with diethyl ether in presence of aluminium chloride, according to Jannasch and Rathjen's method (*Ber.*, 1899, **32**, 2392), and a mixture of the vapour of this compound and hydrogen was passed through a tube containing finely divided nickel and heated to a temperature of 160—170°. A colourless liquid collected in the cooled receiver, which, after purification by fractional distillation, proved to be principally composed of 1:3-*diethyl*cyclo*hexanol*, $CH_2<\begin{matrix} CHEt\cdot CH_2 \\ CHEt\cdot CH_2 \end{matrix}>CH\cdot OH$. This compound is a mobile, colourless liquid, with an odour somewhat like that of peppermint. It boils at 203—205° under atmospheric pressure, and has D_{20}^{20} 0·8945 and n_D 1·46450:

0·1728 gave 0·4851 CO_2 and 0·1915 H_2O. C = 76·6; H = 12·3.
$C_{10}H_{20}O$ requires C = 76·9; H = 12·8 per cent.

The bulk of the diethyl*cyclo*hexanol was boiled for several days under a reflux condenser with anhydrous oxalic acid, and when the dehydration of the alcohol appeared to be complete, the contents of the flask were distilled in a current of steam. A colourless, oily liquid passed over, and was separated from the condensed water by means of ether, while a small quantity of a non-volatile substance was left in the flask. The ethereal solution was dried, the ether removed by distillation, and the remaining liquid fractionally distilled. The principal fraction was redistilled several times over sodium, and finally a liquid of almost constant boiling point was obtained, which gave the following results on analysis:

0·2534 gave 0·8130 CO_2 and 0·2794 H_2O. C = 87·5; H = 12·3.
0·2848 „ 0·9131 CO_2 „ 0·3140 H_2O. C = 87·4; H = 12·3.
$C_{10}H_{18}$ requires C = 87; H = 13 per cent.

It appears from these numbers that the liquid consisted for the most part of **1:3-*diethyl*cyclo*hexene***, $C_{10}H_{18}$, but contained also a little diethyl*cyclo*hexadiene, $C_{10}H_{16}$, from which, owing to the proximity of their boiling points, it could hardly be separated by fractional distillation. The latter was probably derived from a little diethyl*cyclo*hexenol present in the specimen of diethyl*cyclo*hexanol which was used for the preparation. However, it is worth noting in this connexion that, by the action of phosphoric oxide on menthone, Birkenheim (*loc. cit.*) obtained a similar mixture of hydrocarbons which gave on analysis: C = 87·7, 87·8; H = 12·3, 12·4, and drew the conclusion that both the compounds $C_{10}H_{18}$ and $C_{10}H_{16}$ are formed from menthone under the conditions mentioned.

The specimen of diethyl*cyclo*hexene, prepared as described above and apparently not quite pure, was a colourless liquid with a peculiar odour faintly resembling that of the menthene obtained from thymol. It boils at 163—166° under atmospheric pressure, and has D_{20}^{20} 0·83141 and n_D 1·46519. Taking into account its mode of formation, it is obviously the Δ^4-isomeride,

$$CH_2{<}{\begin{array}{l}CHEt{\cdot}CH_2\\CHEt{-}CH\end{array}}{>}CH.$$

The non-volatile residue from the steam distillation of the dehydration product probably consisted of diethyl*cyclo*hexyl oxalate. It was extracted by means of ether, and, after removal of the ether, the oily liquid which remained was subjected to distillation, with the result that it underwent decomposition and yielded more of the hydrocarbon.

The next step was to prepare *diethyl*cyclo*hexene dibromide*, $C_{10}H_{18}Br_2$, and to eliminate two molecules of hydrogen bromide from one molecule of this compound. A cooled solution of bromine (1 mol.) in glacial acetic acid was slowly added to an ice-cold solution of diethyl*cyclo*hexene (1 mol.) in the same solvent. After a short time the solution was poured into water, and the dibromide which separated was collected and washed with water. It is a heavy, colourless, oily liquid, which begins to decompose on keeping. The dibromide was heated on the water-bath under a reflux condenser with excess of alcoholic potassium hydroxide, and when the reaction appeared to be completed steam was passed through the mixture. The oily liquid which passed over was extracted from the condensed water by means of light petroleum, the extract dried, the light petroleum removed by distillation, and the residual liquid fractionally distilled. The principal fraction was purified by

repeated distillation over sodium, and finally a liquid of constant boiling point was obtained, which analysis proved to be the desired hydrocarbon:

0·1143 gave 0·3699 CO_2 and 0·1196 H_2O. C=88·3; H=11·6.
$C_{10}H_{16}$ requires C=88·2; H=11·8 per cent.

The 1:3-*diethyl*cyclo*hexadiene*, $C_{10}H_{16}$, thus obtained is a colourless liquid with a pleasant odour, and has the following constants, boiling point 166—168° under atmospheric pressure, D_{25}^{20} 0·8659 n_D 1·47575. The figure for the specific gravity is perhaps incorrect, as the quantity of material was too small for an accurate determination. The hydrocarbon is unsaturated, reducing at once an alkaline solution of potassium permanganate, and uniting additively with bromine. It also appears to resinify on exposure to the air. Since it is formed by elimination of hydrogen bromide from the dibromide of 1:3-diethyl-Δ^4-*cyclo*hexene (I), it most probably is 1:3-diethyl-$\Delta^{3:5}$-*cyclo*hexadiene (II):

$$CH_2<\begin{matrix}CHEt-CH_2\\ CHEt\cdot CHBr\end{matrix}>CHBr \quad\longrightarrow\quad CH_2<\begin{matrix}CHEt\cdot CH\\ CEt=CH\end{matrix}>CH$$

(I.) (II.)

It is our intention to examine more fully the character of this hydrocarbon and of some of its isomerides.

We take this opportunity of expressing our thanks to the Carnegie Trustees for a grant which defrayed most of the expense of this work.

CHEMISTRY DEPARTMENT,
THE GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

CCXLIV.—*The Velocity of Addition of Alkyl Bromides to Cyclic Tertiary Bases.*

By FRANK STEVENSON LONG.

DURING the last twenty years many investigations have been carried out on the reactivity of various alkyl halides. Summaries of these will be found in Burke and Donnan's paper (Trans., 1904, **85**, 555), showing that the reactivity of the halide exhibits in general no simple relation to its chemical constitution. Much of the more recent research was foreshadowed by the work of Lengfeld (*Amer. Chem. J.*, 1889, **11**, 40), in which the orders of stability towards alkalis on the one hand, and towards silver nitrate and nitric acid

on the other, were contrasted. The relative stabilities in ascending order of magnitude were given as:

(1) Towards alkalis: ethyl, propyl, butyl, *iso*amyl, *iso*butyl, and *iso*propyl.

(2) Towards silver nitrate and acids: *iso*propyl, ethyl, propyl, butyl, *iso*amyl, and *iso*butyl.

These relationships have, in the main, been confirmed by more recent work. As the second order seemed to be the more general, Lengfeld inclined to the belief that the protective influence of the $\cdot CHMe_2$ group apparent in the reactions of *iso*amyl, *iso*butyl, and *iso*propyl compounds towards alkalis was merely a coincidence.

In view of the discovery by Burke and Donnan (*Zeitsch. physikal. Chem.*, 1909, **69**, 148) that the reaction between silver nitrate and alkyl halides is not a simple bimolecular one, it seemed possible that the former series of stabilities (that is, towards alkalis) might be the more normal one, and that the eccentricity of the *iso*propyl compound might be due to some action other than simple replacement of the halogen.

Seeing that the number of velocity constants of addition of cyclic tertiary bases to alkyl halides determined by Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 411) was small compared with the number determined, using open-chain secondary and tertiary bases, it was thought most useful to utilise this method of investigating the problem. As it was found that quinoline and pyridine combine at an easily measurable rate below 100° with alkyl bromides in *iso*amyl-alcoholic solution, it was decided to adhere to these conditions throughout.

A few preliminary investigations showed that the reaction was strictly bimolecular, and that the velocity constant was unaltered by the addition of excess of either of the reacting substances.

The velocity constants for these three bromides at 92·5—92·7° are given in the following table:

	*iso*Amyl bromide.	*iso*Butyl bromide.	*iso*Propyl bromide.
Pyridine	0·175	0·0246	0·0708
β-Picoline	0·138	0·0178	0·0571
α-Picoline	0·071	0·0127	0·0339
Quinoline	0·022	0·0048	0·0138

Thus, *iso*amyl bromide reacts, on the average, seven times and *iso*propyl bromide three times more rapidly than *iso*butyl bromide.

Before considering this result it will be best to take into account the relative reactivities determined by other workers. In the following table these are expressed approximately, taking the smallest velocity constant in each case as unity.

Observer:	*n*-Propyl.	*iso*Propyl.	*iso*Butyl.	*iso*Amyl.	Reaction with
Wislicenus (*Annalen*, 1882, **212**, 239)	—	2	1	—	Sodioacetoacetic ester
Lengfeld (*Amer. Chem. J.*, 1889, **11**, 40)	4	1	between 1 and 2	2	*N*/10-sodium hydroxide
Brussoff (*Zeitsch. physikal. Chem.*, 1900, **34**, 129)	—	1	1	—	2*N*-alcoholic potassium hydroxide
Slator and Twiss (Trans., 1909, **95**, 93)	16	1	—	—	Sodium thiosulphate
Lengfeld (*loc. cit.*)	3·5	9	1	3	Silver nitrate and nitric acid
Burke and Donnan (Trans., *loc. cit.*)	8	enormously large	1	4	Alcoholic silver nitrate
Menschutkin (*J. Russ. Phys. Chem. Soc.*, 1892, **22**, 346)	10	1	2	—	Triethylamine
Wedekind (*Annalen*, 1901, **90**, 116)	3·6 *	1·8 *	1 *	—	Dimethylaniline
Present communication	14	3	1	7	—

* These represent relative percentage yields. In some cases the iodides were used.

All the anomalies in the above table will be seen to be due to the *iso*propyl compound. This is perhaps not so very remarkable, seeing that it differs from the others by being a secondary compound; its reactivity towards pyridine is indeed slightly less than that of the bromide of methylhexylcarbinol, the only other secondary bromide examined.

For the other alkyl compounds we have the reactivity increasing normally as the halogen atom is removed from the influence of the two methyl groups.

The bases examined exhibit steric influences in a remarkably regular manner. With every halogen compound employed the reactivities of the various bases are in the same relative order, the relationships being in many cases almost quantitative. This order, commencing with the most reactive, is: Pyridine, β-picoline, α-picoline, lutidine, quinoline, and 2-methylquinoline.

Experimental.

The *iso*amyl alcohol used as solvent was Kahlbaum's "Pyridine-free" quality. The final adjustment of volume was made after the graduated flasks had been immersed in the thermostat for some time. Times were therefore reckoned from that of the first titration. At definite intervals of time one-tenth of the volume was withdrawn by a warmed pipette, and the reaction arrested by adding cold distilled water. Volhard's thiocyanate method was found to be the most convenient.

The values of the velocity constant were determined from the formula for a bimolecular reaction, namely:

$$\frac{1}{(\theta_2-\theta_1)}\left(\frac{1}{T_\infty - T_{\theta_2}} - \frac{1}{T_\infty - T_{\theta_1}}\right) \times F = k,$$

where θ_1, θ_2 are the times in hours, and T_∞ is the calculated titration value when the action was complete.

The titration numbers are converted into normality figures by multiplying by the appropriate factor F.

The Effect of Excess of each Reacting Substance.

92° in thermostat. *iso*Amyl bromide (b. p. 117·5—118·5°) and pyridine (b. p. 114·1—114·5°).

I 3·02 Grams of *iso*amyl bromide. 1·58 Grams of pyridine. Made up to 100 c.c. with *iso*amyl alcohol.

θ	0	0·33	1·25	3·25	6·50	8·00
20 – T	—	19·91	19·25	17·90	16·05	15·70
k	—	—	0·176	0·181	0·189	0·170

Mean $k=0·179$

II. 6·04 Grams of *iso*amyl bromide. 1·58 Grams of pyridine in 100 c.c.

θ	0	0·25	3·25	6·50	8·00
20 – T	—	19·89	16·50	13·90	12·20
k	—	—	0·170	0·140	0·170

Mean $k=0·170$ (omitting 2nd).

III. 3·02 Grams of *iso*amyl bromide. 3·16 Grams of pyridine in 100 c.c.

θ	0	3·25	6·50	8·0
20 – T	19·89	16·00	13·60	11·85
k	—	0·180	0·162	0·180

Mean $k=0·174$.

These results were sufficient to show that the presence of excess of either of the constituents has no abnormal influence on the velocity of the reaction. The constants for II and III were obtained from the formula:

$$\frac{1}{\theta_2-\theta_1}\left(\log\frac{a-x_2}{b-x_2} - \log\frac{a-x_1}{b-x_1}\right) = (a-b)k.$$

Determination of the Order of the Reaction.

IV. 3·02 Grams of *iso*amyl bromide. 1·58 Grams of pyridine in 100 c.c. Temperature 94—95° in water-bath.

θ	0	1·5	2·5	2·83	16·6
$20-T$	20·0	18·8	18·08	17·95	11·5
k	—	0·195	0·214	0·207	0·206

Mean $k=0·204$.

V. 3·02 Grams of *iso*amyl bromide. 1·58 Grams of pyridine in 50 c.c. 5 C.c. each titration.

θ	0	1·5	2·5	3·5	5	18·5	22
$20-T$...	20·0	17·94	16·85	15·91	14·70	7·96	7·15
k	—	0·191	0·187	0·184	0·180	0·205	0·204

Mean $k=0·192$.

(*a*) *Calculation of the Order by van't Hoff's Method.*—Using the change during the first 1·5 hours in each case for dC/dt we have

$$\text{Order of reaction, } n=\frac{\log\frac{dC_1}{dt}-\log\frac{dC_2}{dt}}{\log\frac{C_1}{C_2}}=1·8 \text{ nearly.}$$

This method is seriously affected by the errors of experiment.

(*b*) *Using the Formula of Noyes* (*Zeitsch. physikal. Chem.*, 189[illegible], **19**, 599):

$$n=1+\frac{\log\theta_1-\log\theta_2}{\log C_{20}-\log C_{10}},$$

where θ_1 and θ_2 are the times for the same fractional part of the reaction to be completed when the initial concentrations are C_{10} and C_{20} respectively. A mean value of $n=1·90$ was obtained graphically.

The reaction may therefore be regarded as strictly bimolecular.

The velocity determinations given below were carried out, except where otherwise stated, at 92·6° in a thermostat; the concentrations were varied from $N/5$ to $4N/5$ in order to keep the velocity between measurable limits. As above, θ represents the time interval in hours, T the titration value in c.c. of $N/10$-silver nitrate, and k the velocity constant. In experiments VII and VIII the value of the velocity constant at 92·6° was obtained by multiplying the value at 91·5° by the known ratio of the values for pyridine and *iso*amyl bromide at these temperatures.

VI. iso*Amyl Bromide and Pyridine* ($2N/5$).

θ	0	1	2	3	4·06	5	7·25
$1/20-T$	0·05311	0·05650	0·06053	0·06378	0·06812	0·07168	0·08136
k	—	0·170	0·185	0·182	0·186	0·186	0·170

Mean value of $k=0·180$.

VII. *iso*A*myl Bromide and* α-*Picoline* (*N*/5) *at* 91·5°.

t	0	2·00	3	6·25	7·33	7·75	23·41
$20-T$ ...	19·70	19·20	18·95	18·19	18·03	17·80	15·07
k	—	0·066	0·0676	0·0674	0·0641	0·0699	0·0690

Mean value of $k=0·0673$. Hence at 92·6° = 0·071.

VIII. *iso*A*myl Bromide and* β-*Picoline* (*N*/5) *at* 91·5°

t	0	2	3·25	6·25	7·3	8·25
$20-T$ ...	19·82	18·85	18·27	16·99	16·77	16·50
k	—	0·132	0·1309	0·1353	0·1265	0·1244

Mean value of $k=0·1298$ ∴ Value at 92·6° = 0·138.

IX. *iso*A*myl Bromide and Quinoline* (4*N*/5) *at* 92·6°.

t	0	2	16	17	25	39	49·6
$1/(20-T)$ ...	0·05200	1 05376	0·06549	0·06645	0·07675	0·09242	0·10427
k	—	0·0220	0·0203	0·0205	0·0238	0·0250	0·0214

Mean value of $k=0·0222$.

X. *iso*B*utyl Bromide and* β-*Picoline* (2*N*/5).

t	0·66	15·7	17·2	23·7
$1/(10-T)$	0·1044	0·1151	0·1164	0·1203
k	—	0·0178	0·0182	0·0173

Mean value of $k=0·0178$.

XI. *iso*B*utyl Bromide and Pyridine* (2*N*/5).

t	0	0·5	4·25	5·5	7	22·5	43·5
$1/(10-T)$ ..	0·1318	0·1321	0·1366	0·1389	0·1406	0·1563	0·1805
k	—	—	0·023	0·0258	0·0250	0·0220	0·0224

Mean value of $k=0·0246$.

XII. *iso*B*utyl Bromide and* α-*Picoline* (2*N*/5).

t	0	12	23·16	24·0
$1/(10-T)$	0·1031	0·1093	0·1149	0·1149
k	—	0·0130	0·0127	0·0125

Mean value of $k=0·0127$.

XIII. *iso*B*utyl Bromide and Quinoline* (4*N*/5).

t	0	2·5	3·0	4	18·1	28·1
$1/(20-T)$	0·05277	0·05325	0·05333	0·05350	0·05621	0·05817
k	—	0·0048	0·0047	0·0046	0·0048	0·0049

Mean value of $k=0·0048$.

XIV. *iso*P*ropyl Bromide and Pyridine* (2*N*/5).

t	0	0·56	1	3	4	5	6
$1/(10-T)$ ...	0·10137	0·10289	0·10411	0·11012	0·11270	0·11559	0·11872
k	—	0·0690	0·0685	0·0727	0·0708	0·0711	0·0725

Mean value of $k=0·0708$.

XV. *iso*Propyl Bromide and α-Picoline (2N/5).

θ	0	1·05	3	4	5	6	25
1/10 − T...	0·10152	0·10280	0·10554	0·10707	0·10883	0·11050	0·1[illegible]
k	—	0·0305	0·0335	0·0347	0·0365	0·0372	0·0[illegible]

Mean value of $k = 0·0339$.

XVI. *iso*Propyl Bromide and β-Picoline (2N/5).

θ...............	0	1·5	2	3·33	4·33	5
1/10 − T	0·10063	0·10421	0·10494	0·10819	0·11080	0·11[illegible]
k	—	0·0596	0·0540	0·0567	0·0585	0·0[illegible]

Mean value of $k = 0·0571$.

XVII. *iso*Propyl Bromide and Quinoline (4N/5).

θ	0	1	2	3	4	22	25
1/20 − T...	0·05016	0·05071	0·05118	0·05171	0·05227	0·06313	0·06[illegible]
k	—	0·0137	0·0128	0·0129	0·0132	0·0147	0·01[illegible]

Mean value of $k = 0·0138$.

In these experiments with *iso*propyl bromide (b. p. 59·5—6 there are indications of a tendency for the "velocity constant increase with time. With the far more reactive propyl brom (b. p. 70—71°) this tendency was very pronounced, especially w the base was also rather volatile; for example, with the sligh volatile quinoline we have:

XVIII. n-Propyl Bromide and Quinoline (2N/5).

θ	0	19·43	20·63	21·9	71·4
1/10 − T...........	0·1011	0·1543	0·1580	0·1631	0·39[illegible]
k	—	0·0685	0·0690	0·0708	0·1[illegible]

whilst with pyridine:

XIX. Propyl Bromide and Pyridine (2N/5).

θ	1·02	3	4·03	7·02	7·50	8·5
1/10 − T ...	0·1155	0·1495	0·1712	0·2421	0·2625	0·29[illegible]
k	0·388	0·412	0·445	0·501	0·562	0·66

The effect would appear to be due to a concentrated film of t reacting substances in the unfilled portion of the flask. This f would become larger as the volume of solution remaining becan less, so that the reaction would seem to increase in velocity as four If this explanation be correct, it would indicate that no serio error due to this cause resulted in the other experiments where remained practically constant.

2-Methylquinoline (b. p. 244—245°) reacted so slowly that or

the commencement of its reactions could be followed. Figures were thus obtained which are, however, for this reason untrustworthy; thus with *iso*amyl bromide:

XX. iso*Amyl Bromide and* 2-*Methylquinoline* (4*N*/5).

t	0·5	14·75	25·5	26
$1/20-T$	0·05053	0·05319	0·05562	0·05571
k	—	0·0047	0·0050	0·0051

The mean value for k (0·0049) gives an indication of the relative velocity. The following determinations are given for comparative purposes:

XXI. sec-*Octyl Bromide and Pyridine* (2*N*/5).

t	0	2·33	4	5	18·4
$1/10-T$	0·1018	0·1096	0·1159	0·1191	0·1712
k	—	0·084	0·088	0·0865	0·94

Mean value for $k=0·088$.

XXII. iso*Amyl Iodide* (*N*/5) *and Pyridine* (2*N*/5).

t	0	0·5	1·5	2·6	7·2
T	0·10	0·43	0·87	1·39	2·86
k	—	0·357	0·301	0·310	0·348

Where $k=2·303\times\frac{5}{\theta_2-\theta_1}\left(\log_{10}\frac{10-T_2}{5-T_2}-\log_{10}\frac{10-T_1}{5-T_1}\right)$.

Mean value of $k=0·329$.

XXIII. iso*Amyl Chloride and Pyridine* (4*N*/5).

t	0	18·7	19	22·5	28
$1/20-T$	0·05005	0·05583	0·05627	0·05698	0·05879
k	—	0·0077	0·0081	0·0077	0·0079

Mean value of $k=0·00785$.

I desire, in conclusion, to express my indebtedness to Professor J. T. Hewitt for kind interest and valuable advice. My thanks are also due to the Research Fund Committee of the East London College for a grant which defrayed the cost of the materials employed.

East London College.

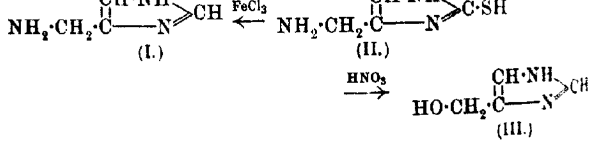
CCXLV.—*Aminoalkylglyoxalines.*

By Frank Lee Pyman.

In view of the great physiological activity of 4(or 5)-β-aminoethyl-glyoxaline (compare Dale and Laidlaw, *J. Physiol.*, 1910, **41**, 318), the preparation of several of its homologues has been carried out, and these have been physiologically tested by Dr. P. P. Laidlaw of the Wellcome Physiological Research Laboratories, to whom the author is indebted for the results given in this paper. In this connexion the recent preparation of other homologues of this base by Ewins (this vol., p. 2052) may be noted.

Barger and Dale (*J. Physiol.*, 1910, **41**, 19), in dealing with the relationship between the chemical constitution of the amines and their physiological action, have shown that the activity varies greatly with the length of the side-chain; in the fatty series the maximum of activity is attained at hexylamine, whilst the most active phenylalkylamine is phenylethylamine, having a fatty side-chain of two carbon atoms. It appeared, therefore, of interest to determine the optimum length of side-chain for physiological effect in the aminoalkylglyoxalines. For comparison with 4(or 5)-β-amino-ethylglyoxaline, 4(or 5)-aminomethylglyoxaline and 4(or 5)-γ-amino-propylglyoxaline were required, but since the latter was not readily accessible its methyl homologue, 4(or 5)-γ-aminobutylglyoxaline, was prepared and tested in its place. Compared with 4(or 5)-β-amino-ethylglyoxaline, the activity of these bases proved to be negligible.

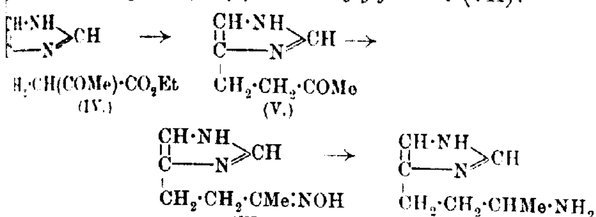
4(or 5)-Aminomethylglyoxaline (I) has recently been described by Windaus and Opitz (*Ber.*, 1911, **44**, 1721), who prepared it by Curtius' method from glyoxaline-4(or 5)-acetic acid obtained from histidine. It may, however, readily be prepared synthetically by suitably oxidising 2-thiol-4(or 5)-aminomethylglyoxaline (II). It has previously been shown (this vol., p. 669) that the customary method of oxidising thiolglyoxalines to glyoxalines by means of nitric acid leads, in the case of this compound, to 4(or 5)-hydroxymethylglyoxaline (III). If, however, an oxidising agent not producing nitrous acid were employed, the formation of 4(or 5)-aminomethylglyoxaline would be possible. Other oxidising agents were therefore tried, and



It was found that ferric chloride in calculated quantity oxidised 2-thiol-4(or 5)-aminomethylglyoxaline to 4(or 5)-aminomethylglyoxaline in a yield amounting to more than 50 per cent. of the theoretical.

Potassium permanganate is unsuitable for the oxidation of 2-thiol-4(or 5)-aminomethylglyoxaline to 4(or 5)-aminomethylglyoxaline, for it readily attacks the former substance, causing complete rupture of the glyoxaline ring; cold dilute aqueous solutions of potassium permanganate are immediately decolorised by 2-thiol-4(or 5)-aminomethylglyoxaline, but not by 4(or 5)-aminomethylglyoxaline or other glyoxalines not containing the 2-thiol group. This difference in behaviour is ascribed to the possibility of the thiol base reacting in the tautomeric thiocarbamide form as an unsaturated compound.

4(or 5)-γ-*Aminobutylglyoxaline* was readily prepared as follows: Ethyl 4(or 5)-glyoxalinemethylacetoacetate (IV) (this vol., p. 1392) was converted into the corresponding ketone, 4(or 5)-γ-*ketobutylglyoxaline* (V), by hydrolysis with hydrochloric acid. This was next transformed into the oxime, 4(or 5)-γ-*oximinobutylglyoxaline* (VI), which on reduction by means of sodium amalgam and acetic acid gave 4(or 5)-γ-*aminobutylglyoxaline* (VII):



(IV.) (V.) (VI.) (VII.)

A quantity of αβ-bis[4(or 5)-glyoxaline]-propionitrile (VIII) (this vol., p. 677) which is formed as a by-product in the preparation of 4(or 5)-cyanomethylglyoxaline being available, it was thought of interest to reduce it to βγ-*bis*[4(or 5)-*glyoxaline*]-*propylamine* (IX), which may be regarded as an aminoethylglyoxaline containing a glyoxalinemethyl substituent. This reduction was carried out with sodium and alcohol, and the desired base was obtained, together with another compound, which was probably αβ-*bis*[4(or 5)-*glyoxaline*]-*propionic acid* (X):

$$C_3H_3N_2\cdot CH_2\cdot CH(CN)\cdot C_3H_3N_2 \longrightarrow$$
(VIII.)

$$C_3H_3N_2\cdot CH_2\cdot CH(CH_2\cdot NH_2)\cdot C_3H_3N_2, \text{ and}$$
(IX.)

$$C_3H_3N_2\cdot CH_2\cdot CH(CO_2H)\cdot C_3H_3N_2.$$
(X.)

The physiological action of $\beta\gamma$-bis[4(or 5)-glyoxaline]-propylamine is very slight compared with that of 4(or 5)-β-aminoethylglyoxaline.

The two isomeric *N*-methyl derivatives of 4(or 5)-β-aminoethylglyoxaline in which the methyl group substitutes the imino-hydrogen atom of the glyoxaline ring were next prepared. These compounds, 1-methyl-4(and 5)-aminoethylglyoxaline (XI and XII)

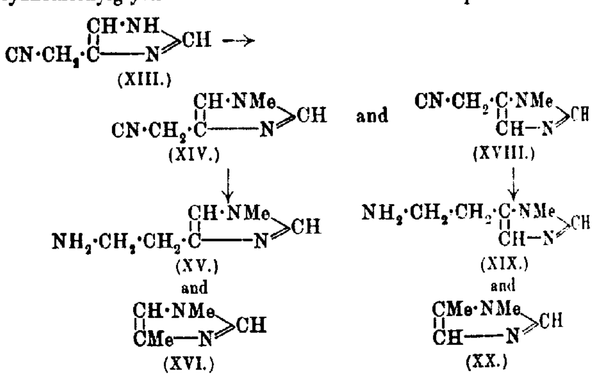
(XI.) (XII.)

were obtained by reduction of the corresponding methylcyanomethylglyoxalines. Their physiological action is negligible compared with that of 4(or 5)-β-aminoethylglyoxaline.

4(or 5)-Cyanomethylglyoxaline (XIII) (this vol., p. 676) yields, on methylation with methyl sulphate and alkali a mixture of the 1:4- and 1:5-methylcyanomethylglyoxalines, from which the former can readily be obtained in a pure state, and the latter less readily by fractional crystallisation of the picrates.

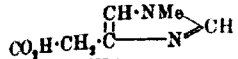
1-*Methyl*-4-*cyanomethylglyoxaline* (XIV) gave on reduction with sodium and alcohol 1-*methyl*-4-β-*aminoethylglyoxaline* (XV), together with small quantities of 1:4-dimethylglyoxaline (XVI) and 1-*methylglyoxaline*-4-*acetic acid* (XVII).

1-*Methyl*-5-*cyanomethylglyoxaline* (XVIII) when similarly treated yielded 1-*methyl*-5-β-*aminoethylglyoxaline* (XIX) and 1:5-dimethylglyoxaline (XX). As the constitution of the 1:4- and 1:5-dimethylglyoxalines has already been determined with a high degree of probability (Trans., 1910, **97**, 1814), orientation of the methylated cyanomethylglyoxalines and their other reduction products follows:

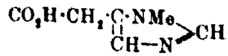


1-Methylglyoxaline-4-acetic acid may readily be prepared by hydrolysing 1-methyl-4-cyanomethylglyoxaline with alkali. Its

ester, *ethyl* 1-*methylglyoxaline*-4-*acetate*, was prepared by the action of alcoholic hydrogen chloride on 1-methyl-4-cyanomethylglyoxaline:



(XVII.)



(XXI.)

1-*Methylglyoxaline*-5-*acetic acid* (XXI) was obtained by hydrolysing 1-methyl-5-cyanomethylglyoxaline with alkali.

Experimental.

Oxidation of 2-*Thiol*-4(or 5)-*aminomethylglyoxaline to* 4(or 5)-*Aminomethylglyoxaline*.

1·29 Grams of 2-thiol-4(or 5)-aminomethylglyoxaline (this vol., p. 672) were dissolved in 50 c.c. of water, added to a solution of 9·8 grams of ferric chloride in 100 c.c. of water, and the mixture digested for half an hour in the water-bath. Thirty c.c. of 10 per cent. aqueous sodium carbonate were then added, followed by a hot solution of 4·6 grams of picric acid in 100 c.c. of boiling water. The liquor was then boiled with a little animal charcoal and filtered, and on cooling 3·2 grams of pure 4(or 5)-aminomethylglyoxaline dipicrate separated in the first crop; this quantity represents 56 per cent. of the theoretical yield.

4(or 5)-Aminomethylglyoxaline dipicrate crystallises from water in hexagonal or diamond-shaped plates, which melt at 210—211° (corr.). It contains $1H_2O$, which is lost at 120°, but not at 100°. The water of crystallisation in this salt is not mentioned by Windaus and Opitz (*Ber.*, 1911, **44**, 1723), who give the melting point as 209°:

0·1749 * lost *nil* at 100°, lost 0·0054 at 120°. $H_2O = 3·1$.

0·2064 † gave 0·2550 CO_2 and 0·0496 H_2O. C = 33·7; H = 2·7.

$C_4H_7N_3,2C_6H_3O_7N_3,H_2O$ requires C = 33·5; H = 2·6; $H_2O = 3·1$ per cent.

4(or 5)-Aminomethylglyoxaline dihydrochloride was prepared by treating the picrate with hydrochloric acid, removing the picric acid by means of ether, evaporating the acid liquor to dryness, and crystallising the residue from water. It separates from water in colourless, prismatic needles, which contain $\frac{1}{2}H_2O$, and after drying at 100° melt at 244—245° (corr.) after sintering from about 235°. Its aqueous solution is strongly acid:

0·1262, air-dried salt, lost 0·0068 at 100°. $H_2O = 5·4$.

$C_4H_7N_3,2HCl,\frac{1}{2}H_2O$ requires $H_2O = 5·0$ per cent.

* Air-dried. † Dried at 100°.

For anhydrous salt: Found, C=28·0; H=5·6. Calc., C=28·; H=5·3 per cent.

Windaus and Opitz (*loc. cit.*), who crystallised this salt from a mixture of methyl alcohol and ether, do not mention any water of crystallisation; they state that on heating, the salt sinters from 23 onwards.

4(or 5)-*Aminomethylglyoxaline hydrogen oxalate* crystallises from water in monoclinic, hexagonal plates, which decompose at 21 (corr.). It is anhydrous, and is sparingly soluble in cold water:

0·2478 gave 0·3158 CO_2 and 0·0898 H_2O. C=34·8; H=4·1.

$C_4H_7N_3,2C_2H_2O_4$ requires C=34·7; H=4·0 per cent.

4(or 5)-γ-*Ketobutylglyoxaline* [4(or 5)-*Glyoxaline-ethyl Methyl Ketone*],

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot \begin{array}{l} CH\cdot NH \\ \| \\ C\text{——}N \end{array}\!\!>CH.$$

Fifteen grams of ethyl 4(or 5)-glyoxalinemethylacetoacetate hydrogen oxalate (this vol., p. 1392) were converted into the base, and this boiled under a reflux condenser for three hours with 60 c.c. of hydrochloric acid and 90 c.c. of water. The liquid was then evaporated to dryness under diminished pressure, and the residue dissolved in a little water, mixed with sodium carbonate, and extracted with chloroform. The extract after drying and distillation of the solvent left the ketone as a viscid, brown oil, which solidified on keeping, forming large, buff crystals, melting at 76—78°, and amounting to 4·4 grams; this yield is 64 per cent. of the theoretical.

4(or 5)-γ-*Ketobutylglyoxaline* crystallises from anhydrous ethyl acetate in stout, colourless, prismatic needles, which melt at 80—81° (corr.). It is very readily soluble in water, alcohol, acetone, or chloroform, readily so in ethyl acetate, and very sparingly so in ether or benzene:

0·1278 gave 0·2854 CO_2 and 0·0882 H_2O. C=60·9; H=7·7.

$C_7H_{10}ON_2$ requires C=60·8; H=7·3 per cent.

The *picrate* crystallises from water or alcohol in fine, yellow needles, which melt at 192—193° (corr.). It is very sparingly soluble in cold water or alcohol, but fairly readily so in hot water:

0·1088 gave 0·1702 CO_2 and 0·0370 H_2O. C=42·6; H=3·8.

$C_7H_{10}ON_2,C_6H_3O_7N_3$ requires C=42·5; H=3·6 per cent.

4(or 5)-γ-*Oximinobutylglyoxaline*,

$$HO\cdot N\!:\!CMe\cdot CH_2\cdot CH_2\cdot \begin{array}{l} CH\cdot NH \\ \| \\ C\text{——}N \end{array}\!\!>CH.$$

This oxime is readily prepared in good yield by heating on the water-bath an aqueous solution of the ketone with the calculated

amounts of hydroxylamine hydrochloride and sodium carbonate; on concentrating and cooling the solution, the oxime crystallises out, and is purified by recrystallisation from water.

4(or 5)-γ-*Oximinobutylglyoxaline* crystallises from water in clear, colourless plates, which melt at 152—153° (corr.). It is sparingly soluble in cold water or acetone, fairly readily so in alcohol or hot water, but very sparingly so in chloroform:

0·2134 gave 0·4284 CO_2 and 0·1407 H_2O. C = 54·7; H = 7·4.

$C_7H_{11}ON_3$ requires C = 54·9; H = 7·3 per cent.

The *picrate* crystallises from water in hard, spherical grains, which melt at 166—168° (corr.). This salt is sparingly soluble in cold, but readily so in hot, water.

4(or 5)-γ-*Aminobutylglyoxaline*,

$$\begin{array}{l} \qquad\qquad\qquad\qquad\qquad\qquad\quad CH\cdot NH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \Vert \qquad\quad > CH. \\ CH_3\cdot CH(NH_2)\cdot CH_2\cdot CH_2\cdot C\text{——}N \end{array}$$

2·3 Grams of 4(or 5)-γ-oximinobutylglyoxaline were dissolved in [illegible] c.c. of alcohol and 5 c.c. of glacial acetic acid. Fifty grams of 3 per cent. sodium amalgam were then added, and the mixture well shaken and cooled with water. Enough water was supplied from time to time to dissolve the separated sodium acetate, and two further quantities, each of 5 c.c., of acetic acid and 50 grams of sodium amalgam were subsequently added. When the sodium amalgam had been used up, the liquor was diluted with about 100 c.c. of water, and poured into a hot solution of 7 grams of picric acid in 200 c.c. of water, when on cooling 4(or 5)-γ-aminobutylglyoxaline dipicrate crystallised out. After recrystallisation from water 4·1 grams of the pure salt were obtained, that is, 45 per cent. of the theoretical.

4(or 5)-γ-*Aminobutylglyoxaline dipicrate* crystallises from water in long, golden, somewhat serrated spikes, which melt at 247° (corr.) to a brown liquid, which then decomposes. This salt is anhydrous, and very sparingly soluble in cold, but fairly readily so in hot, water:

0·1163 gave 0·1638 CO_2 and 0·0350 H_2O. C = 38·4; H = 3·4.

$C_7H_{13}N_3,(C_6H_3O_7N_3)_2$ requires C = 38·2; H = 3·2 per cent.

Reduction of αβ-Bis[4(or 5)-glyoxaline]-propionitrile.

Nine grams of αβ-bis[4(or 5)-glyoxaline]-propionitrile hydrogen malate* were converted into the base in the manner previously described, and this was reduced by means of 5 grams of sodium

* This vol., p. 677; the formula of the base should read $C_9H_9N_5$.

and 75 c.c. of absolute alcohol. The reaction product was neutralised with hydrochloric acid, made strongly alkaline with sodium carbonate, evaporated to dryness under diminished pressure, and the residue completely extracted with absolute alcohol. After the removal of the bulk of the solvent, the extract was poured into a solution of 20 grams of picric acid in 500 c.c. of boiling water, when a viscous oil separated. After the solution had cooled somewhat it was decanted from the oil and filtered, when it deposited about 3 grams of crystals, melting at 195—200°. The very sparingly soluble oil also became crystalline on cooling, and was extracted with 500 c.c. of boiling water, filtered, and allowed to cool to about 50°, when 5·0 grams of orange needles, melting at 150—153°, separated; these were collected, and the mother liquor allowed to become quite cold, when a further 1·6 grams of crystals, melting at about 210°, separated.

The more sparingly soluble picrate was readily purified by crystallisation from water, and proved to be *βγ-bis*[4(or 5)-*glyoxaline*]-*propylamine tripicrate*; 3·4 grams of this salt were obtained in a pure state, decomposing at 158° (corr.), that is, 18 per cent. of the theoretical. The more easily soluble picrate was less readily purified; it melted and decomposed at 218—220° (corr.) when pure, and was probably *αβ-bis*[4(or 5)-*glyoxaline*]-*propionic acid dipicrate*:

0·1300, air-dried salt, lost 0·0072 at 100°. $H_2O = 5·5$.

$C_9H_{10}O_2N_4,(C_6H_3O_7N_3)_2,2H_2O$ requires $H_2O = 5·1$ per cent.

0·1010 * gave 0·1392 CO_2 and 0·0268 H_2O. C = 37·6; H = 3·0.

0·1232 * ,, 0·1706 CO_2 ,, 0·0331 H_2O. C = 37·8; H = 3·0.

$C_9H_{10}O_2N_4,(C_6H_3O_7N_3)_2$ requires C = 37·9; H = 2·4 per cent.

βγ-Bis[4(or 5)-*glyoxaline*]-*propylamine*,
$C_3H_3N_2·CH_2·CH(CH_2·NH_2)·C_3H_3N_2$.

The *tripicrate* crystallises from water in beautiful, orange-yellow, flat needles, which soften from 150° and decompose at 158° (corr.). This salt is sparingly soluble in hot, and very sparingly so in cold, water. It is anhydrous:

0·1330 gave 0·1786 CO_2 and 0·0330 H_2O. C = 36·6; H = 2·8.

$C_9H_{13}N_5,(C_6H_3O_7N_3)_3$ requires C = 36·9; H = 2·5 per cent.

The *trihydrochloride* was prepared by treating the picrate with hydrochloric acid and ether, and after evaporation of the excess of acid was obtained as a colourless varnish. This readily became crystalline when warmed with alcohol. The crystals were collected, dissolved in very little water, and hot alcohol added to the solution,

* Dried at 100°.

when the salt separated in beautiful, colourless, refracting prisms. The air-dried salt contains a molecule of water of crystallisation, which is not lost at 100°, but probably escapes at about 140°, for on heating the salt sinters at this temperature, but then remains unchanged until it melts at 235—237° (corr.). It is readily soluble in water, giving an acid solution, but is insoluble in absolute alcohol:

0·1382 gave 0·1730 CO_2 and 0·0730 H_2O. C = 34·1; H = 5·9.

0·1482 „ 0·1981 AgCl. Cl = 33·1.

$C_7H_{13}N_3,3HCl,H_2O$ requires C = 33·9; H = 5·7; Cl = 33·4 per cent.

Methylation of 4(or 5)-*Cyanomethylglyoxaline.*

Twenty grams of 4(or 5)-cyanomethylglyoxaline (this vol., p. 676) were dissolved in 80 c.c. of 10 per cent. aqueous sodium hydroxide, and shaken with 16 grams of methyl sulphate added gradually while the liquid was shaken and cooled by running water. Another 70 c.c. of 10 per cent. aqueous sodium hydroxide and 16 grams of methyl sulphate were then added. The clear brown liquor was completely extracted by chloroform, and the solvent removed from the extract, when a brown oil resulted. This was dissolved in water, and poured into 2100 c.c. of warm 2 per cent. picric acid solution, when most of the 1-*methyl-4-cyanomethylglyoxaline picrate* crystallised out at once in a pure state. On concentrating the mother liquors, 1-*methyl-5-cyanomethylglyoxaline picrate* separated out, mixed with small quantities of its isomeride, and it was purified by recrystallisation from water.

There were isolated 28·5 grams of 1-methyl-4-cyanomethylglyoxaline picrate, melting at 209—210° (corr.), and 9·9 grams of 1-methyl-5-cyanomethylglyoxaline picrate, melting at 156—157° (corr.), these quantities amounting to 43 and 15 per cent. of the theoretical respectively.

1-*Methyl-4-cyanomethylglyoxaline*, $\begin{matrix} & CH\cdot NMe \\ CN\cdot CH_2\cdot C & \text{——}N \end{matrix} \!\!>\! CH.$

This base crystallises from chloroform in clusters of plates, which melt at 34—36° (corr.). It is very deliquescent, and readily soluble in water and the usual organic solvents, with the exception of ether and light petroleum:

0·1337* gave 0·2917 CO_2 and 0·0731 H_2O. C = 59·5; H = 6·1.

$C_6H_7N_3$ requires C = 59·5; H = 5·8 per cent.

The *hydrogen oxalate* crystallises from water or alcohol in

* Dried at 100°.

prismatic needles, which melt at 116—117° (corr.). It is readily soluble in water, but sparingly so in alcohol:

0·1503 gave 0·2496 CO_2 and 0·0572 H_2O. C=45·3; H=4·3

0·1143 „ 19·6 c.c. N_2 at 18° and 759 mm. N=20·2.

$C_6H_7N_3,C_2H_2O_4$ requires C=45·5; H=4·3; N=19·9 per cent.

The *picrate* crystallises from water in flat, fern-like clusters of stout needles, or in rods of a rather pale yellow colour, which melt at 209—210° (corr.). It is anhydrous, and is very sparingly soluble in cold, but fairly readily so in hot, water:

0·1530 gave 0·2290 CO_2 and 0·0395 H_2O. C=40·8; H=3·0

$C_6H_7N_3,C_6H_3O_7N_3$ requires C=41·1; H=2·9 per cent.

The *mercurichloride* and *mercuri-iodide* both readily crystallise from water in long needles.

1-Methyl-5-cyanomethylglyoxaline, $\begin{matrix}CN\cdot CH_2\cdot C\cdot NMe \\ \quad\quad\quad \| \\ \quad\quad\quad CH-N\end{matrix}\!\!>\!CH$.

This base was obtained as an oil, which did not crystallise when kept for several hours at 0°. It is readily soluble in water, alcohol, or chloroform.

The *hydrogen oxalate* crystallises from alcohol in prisms, which sinter slightly from 135°, and melt and effervesce at 139—140° (corr.). It is anhydrous. It is readily soluble in water, but sparingly so in alcohol:

0·1580 gave 0·2632 CO_2 and 0·0612 H_2O. C=45·4; H=4·3.

$C_6H_7N_3,C_2H_2O_4$ requires C=45·5; H=4·3 per cent.

The *picrate* crystallises from water in large, pale yellow, glistening leaflets, which melt at 156—157° (corr.). This salt is anhydrous, sparingly soluble in cold, but readily so in hot, water:

0·1507 gave 0·2284 CO_2 and 0·0411 H_2O. C=41·3; H=3·1.

$C_6H_7N_3,C_6H_3O_7N_3$ requires C=41·1; H=2·9 per cent.

1-Methylglyoxaline-4-acetic Acid, $\begin{matrix}\quad\quad\quad\quad\quad CH\cdot NMe \\ \quad\quad\quad\quad\quad \| \\ CO_2\cdot H\cdot CH_2\cdot C\text{——}N\end{matrix}\!\!>\!CH$.

0·75 Gram of 1-methyl-4-cyanomethylglyoxaline was dissolved in 20 c.c. of water, and boiled with 10 c.c. of 10 per cent. aqueous sodium hydroxide until no more ammonia was evolved. Then 9 c.c. of 10 per cent. hydrochloric acid were added, followed by 1·5 grams of picric acid in 40 c.c. of boiling water. On cooling 1·5 grams of 1-*methylglyoxaline-4-acetic acid picrate* separated in large, striated prisms, melting at 187—189° (corr.), and a further 0·4 gram equally pure was obtained on concentrating the mother liquor, the yield thus amounting to 83 per cent. of the theoretical

0·1209 gave 0·1751 CO_2 and 0·0332 H_2O. C = 39·5; H = 3·1.

$C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C = 39·0; H = 3·0 per cent.

Ethyl 1-*Methylglyoxaline*-4-*acetate*, $C_4H_5N_2·CH_2·CO_2Et$.

Eight grams of 1-methyl-4-cyanomethylglyoxaline picrate were converted into the base, and this boiled for two hours with 50 c.c. of 15 per cent. absolute alcoholic hydrogen chloride, when ammonium chloride separated. The mixture was evaporated to dryness under diminished pressure, dissolved in water, mixed with sodium carbonate, and extracted with chloroform, when ethyl 1-methylglyoxaline-4-acetate was obtained as a brown oil. This was converted into the picrate, and purified by crystallisation from water, when 4·2 grams of the pure salt were obtained, that is, 46 per cent. of the theoretical.

Ethyl 1-*methylglyoxaline*-4-*acetate picrate* crystallises from water in long, yellow fibres, having the appearance of glass wool. It is very sparingly soluble in cold, but readily so in hot, water. It melts at 133—134° (corr.):

0·1092 * gave 0·1700 CO_2 and 0·0370 H_2O. C = 42·4; H = 3·8.

$C_8H_{12}O_2N_2,C_6H_3O_7N_3$ requires C = 42·3; H = 3·8 per cent.

1-*Methylglyoxaline*-5-*acetic Acid*, $\begin{array}{l}CO_2H·CH_2·C·NMe \\ \qquad\qquad\quad \| \\ \qquad\qquad CH—N\end{array}\!\!>\!CH$.

This compound was prepared by hydrolysis of its nitrile, and isolated as the *picrate*. This salt crystallises from water in beautiful, hexagonal plates, which melt at 180—181° (corr.), after sintering a few degrees earlier. It is anhydrous and sparingly soluble in cold, but readily so in hot, water:

0·1200 gave 0·1732 CO_2 and 0·0358 H_2O. C = 39·4; H = 3·3.

$C_6H_8O_2N_2,C_6H_3O_7N_3$ requires C = 39·0; H = 3·0 per cent.

Reduction of 1-*Methyl*-4-*cyanomethylglyoxaline*.

Seven grams of 1-methyl-4-cyanomethylglyoxaline were reduced by means of 10 grams of sodium and 100 c.c. of absolute alcohol. The reaction product was acidified with hydrochloric acid, made strongly alkaline with sodium carbonate, evaporated to dryness under diminished pressure, and the residue extracted with alcohol. The alcoholic extract was evaporated to dryness, and the residue extracted successively with ether, ethyl acetate, and absolute alcohol.

The ethereal extract amounted to 3·0 grams; it was dissolved

* Dried at 100°.

in water, and poured into a litre of warm 1 per cent. aqueous picric acid, when 6·6 grams of 1-*methyl-4-β-aminoethylglyoxaline dipicrate* separated in a pure state on cooling. The mother liquor was extracted with ether to remove free picric acid and evaporated to low bulk, when about 0·5 gram of a crude picrate, melting at about 140°, separated. After several crystallisations from water, a very small amount of 1:4-dimethylglyoxaline picrate was isolated from it, but was not obtained quite pure. This salt melted at 162—163° (corr.), the pure salt (Trans., 1910, 97, 1819), melting at 167—168° (corr.) in the same bath, whilst a mixture of the two melted at 162—163° (corr.), and a mixture of this salt with 1:5-dimethylglyoxaline picrate at 135—140°.

The ethyl acetate extract afforded a further 1·3 grams of pure 1-methyl-4-β-aminoethylglyoxaline dipicrate, so that the total yield of this compound amounted to 7·9 grams, that is, 23 per cent. of the theoretical.

The absolute alcohol extract gave, with picric acid, at first an amorphous precipitate, but later a small quantity of 1-methylglyoxaline-4-acetic acid picrate.

1-*Methyl-4-β-aminoethylglyoxaline*,

$$\begin{array}{l} \qquad\qquad\qquad\quad CH\cdot NMe \\ \qquad\qquad\qquad\quad \| \qquad\qquad > CH. \\ NH_2\cdot CH_2\cdot CH_2\cdot C\text{——}N \end{array}$$

The *dipicrate* crystallises from water in large, flat needles, which melt at 217° (corr.). It is very sparingly soluble in cold water and is anhydrous:

0·1803 gave 0·2468 CO_2 and 0·0498 H_2O. C=37·3; H=3·1.

$C_6H_{11}N_3,(C_6H_3O_7N_3)_2$ requires C=37·0; H=2·9 per cent.

The *dihydrochloride* was prepared from the dipicrate by means of hydrochloric acid and ether. It crystallises from absolute alcohol in colourless prisms, which melt at 204—206° (corr.), after drying at 100°. It is deliquescent, and readily soluble in water, but sparingly so in absolute alcohol:

0·1186 * gave 0·1596 CO_2 and 0·0708 H_2O. C=36·7; H=6·7.

$C_6H_{11}N_3,2HCl$ requires C=36·4; H=6·6 per cent.

Reduction of 1-*Methyl-5-cyanomethylglyoxaline. Formation of* 1-*Methyl-5-β-aminoethylglyoxaline.*

Three grams of 1-methyl-5-cyanomethylglyoxaline were reduced by means of sodium and alcohol, and the products worked up as in the case of the 1:4-compound.

The combined ethereal and ethyl acetate extracts gave first an amorphous picrate, then small quantities of 1-*methyl-5-β-amino-*

ethylglyoxaline dipicrate, which formed yellow needles, melting at 201° (corr.), after drying at 100°:

0·1181 * gave 0·1615 CO_2 and 0·0305 H_2O. C=37·3; H=2·9.

$C_4H_{11}N_2,(C_6H_3O_7N_3)_2$ requires C=37·0; H=2·9 per cent.

The mother liquor from this salt then gave a small quantity of 1 : 5-dimethylglyoxaline picrate in clusters of slender needles, melting at 167—168° (corr.):

0·0907 gave 0·1345 CO_2 and 0·0267 H_2O. C=40·4; H=3·3.

$C_5H_8N_2,C_6H_3O_7N_3$ requires C=40·6; H=3·4 per cent.

This salt was identified by determination of the melting points of its mixtures with pure 1 : 4- and 1 : 5-dimethylglyoxaline picrates (Trans., 1910, **97**, 1819), when it was found that the mixture with the 1 : 4-salt melted at 135—140°, whilst that with the 1 : 5-salt still melted at 167—168° (corr.).

The alcoholic extract gave a very small quantity of a crystalline picrate which melted at 162—175°; it was probably impure methylglyoxaline-5-acetic acid picrate, but the quantity obtained was insufficient for identification.

THE WELLCOME CHEMICAL WORKS,
DARTFORD, KENT.

CXLVI.—*The Probable Cause of the Elimination of a Carbethoxyl Group as Ethyl Carbonate by the Action of Sodium Ethoxide.*

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

SEVERAL instances have now been recorded in which the passage of an open-chain δ-cyanoethyl salt into an imino-derivative of *cyclo*pentane through the agency of cold alcoholic sodium ethoxide is accompanied by the elimination of a carbethoxy-group as ethyl carbonate. It is sufficient for our purpose to select two examples of this type of reaction from the recent experiments of Mitchell and Thorpe (Trans., 1910, **97**, 2261) on the formation of imino-derivatives of α-hydrindone. It was then shown that ethyl *o*-cyanobenzylmalonate (I) was transformed into ethyl 1-iminohydrindene-2-carboxylate (II), and that ethyl α-*o*-dicyano-β-phenylpropionate (III) was converted into 1-imino-2-cyanohydrindene (IV).

It was suggested that these and other reactions of the same kind

* Dried at 100°.

might be due to spatial conditions, and that, in the five-membered ring, the presence of two groups of large molecular volume attached

$$C_6H_4{<}\begin{array}{l}CN\\CH_2{\cdot}CH(CO_2Et)_2\end{array} + EtOH \rightarrow$$
(I.)

$$C_6H_4{<}\begin{array}{l}C(:NH)\\CH_2\text{——}\end{array}{>}CH{\cdot}CO_2Et + CO(OEt)_2$$
(II.)

$$C_6H_4{<}\begin{array}{l}CN\\CH_2{\cdot}CH(CN){\cdot}CO_2Et\end{array} + EtOH \rightarrow$$
(III.)

$$C_6H_4{<}\begin{array}{l}C(:NH)\\CH_2\text{——}\end{array}{>}CH{\cdot}CN + CO(OEt)_2$$
(IV.)

to any one carbon atom might not be a condition of stability, and consequently, when the compound was treated by a suitable reagent, one of these groups was eliminated.

An examination of the facts shows that several derivatives of the five-carbon ring are known which have more than one carbethoxyl group attached to any one carbon atom, such as, for example, ethyl *cyclo*pentane-1 : 1 : 3 : 3-tetracarboxylate (V) and ethyl hydrindene-2 : 2-dicarboxylate (VI):

$$\begin{array}{l}CH_2{\cdot}C(CO_2Et)_2\\CH_2{\cdot}C(CO_2Et)_2\end{array}{>}CH_2 \qquad C_6H_4{<}\begin{array}{l}CH_2\\CH_2\end{array}{>}C(CO_2Et)_2$$
(V.) (VI.)

If our hypothesis is correct, these compounds should pass, on treatment with sodium ethoxide, into ethyl carbonate and the corresponding ethyl esters, thus:

$$\begin{array}{l}CH_2{\cdot}C(CO_2Et)_2\\CH_2{\cdot}C(CO_2Et)_2\end{array}{>}CH_2 + 2EtOH \rightarrow$$

$$\begin{array}{l}CH_2{\cdot}CH(CO_2Et)\\CH_2{\cdot}CH(CO_2Et)\end{array}{>}CH_2 + 2CO(OEt)_2$$

and

$$C_6H_4{<}\begin{array}{l}CH_2\\CH_2\end{array}{>}C(CO_2Et)_2 + EtOH \rightarrow$$

$$C_6H_4{<}\begin{array}{l}CH_2\\CH_2\end{array}{>}CH{\cdot}CO_2Et + CO(OEt)_2$$

We have therefore prepared these compounds, the former by Pospischill's method (*Ber.*, 1898, **31**, 1950) from the disodium derivative of ethyl butanetetracarboxylate by the action of methylene iodide, and the latter by v. Baeyer and Perkin's method (*Ber.*, 1884, **17**, 122) from *o*-xylylene dibromide and ethyl sodiomalonate.

We find that both these esters are quite unacted on by cold alcoholic sodium ethoxide. It is evident, therefore, that the

influences causing the elimination of the carbethoxyl group prior to the formation of the five-ring imino-compounds cannot be ascribed to spatial conditions or to the over-weighting of any one carbon atom of the ring. A careful review of the facts showed, moreover, that the displacement of the carbethoxy-group by sodium in the manner illustrated by the equation:

$$C_6H_4{<}\begin{matrix}CN\\CH_2\cdot CH(CO_2Et)_2\end{matrix} \rightarrow C_6H_4{<}\begin{matrix}C(:NH)\\CH_2\end{matrix}{>}C(CO_2Et)_2 + NaOEt \rightarrow$$
$$C_6H_4{<}\begin{matrix}C(:NH)\\CH_2\end{matrix}{>}CNa\cdot CO_2Et + CO(OEt)_2$$

could not be the determining cause of this reaction, because, *inter alia*, ethyl 1-iminohydrindene-2-carboxylate (II) and analogously constituted compounds do not react with sodium ethoxide to form sodium derivatives. Finally, we decided to compare the various classes of compounds in which this reaction had been noticed, and ultimately arrived at an explanation, which forms the subject of the present communication.

During some experiments on the constitution of glutaconic acid (Trans., 1905, **87**, 1681) it was found that ethyl α-cyano-αβγ-trimethylglutaconate (VII) when treated with sodium ethoxide was converted into ethyl α-cyano-αβγ-trimethylcrotonate (VIII) and ethyl carbonate, thus:

$$\underset{\text{(VII.)}}{CO_2Et\cdot CMe\!:\!CMe\cdot CMe(CN)\cdot CO_2Et} + EtOH \rightarrow$$
$$\underset{\text{(VIII.)}}{CO_2Et\cdot CMe\!:\!CMe\cdot CHMe\cdot CN} + CO(OEt)_2.$$

A comparison of ethyl α-cyano-αβγ-trimethylglutaconate (VII) with the normal ring-compound from ethyl *o*-cyanobenzylmalonate (Ia) shows that these substances have one important point in common, namely, that it is necessary for each of them to part with the carbethoxyl group before the hydrogen atom necessary to permit the substance to react in its tautomeric form can be acquired, thus:

$$\underset{\text{(Ia.)}}{C_6H_4{<}\begin{matrix}C(:NH)\\CH_2\end{matrix}{>}C(CO_2Et)_2} \rightarrow \begin{matrix}C_6H_4{<}\begin{matrix}C(:NH)\\CH_2\end{matrix}{>}CH\cdot CO_2Et\\ C_6H_4{<}\begin{matrix}C(NH_2)\\CH_2\end{matrix}{\geqslant}C\cdot CO_2Et\\ \text{(Tautomeric forms.)}\end{matrix}$$

$$\underset{\text{(VII.)}}{CO_2Et\cdot CMe\!:\!CMe\cdot CMe(CN)\cdot CO_2Et} \rightarrow \begin{matrix}CO_2Et\cdot CMe\!:\!CMe\cdot CHMe\cdot CN\\ CO_2Et\cdot CHMe\cdot CMe\!:\!CMe\cdot CN\\ \text{(Tautomeric forms.)}\end{matrix}$$

This view at once suggests a close relationship between compounds having the complex HC·C:C and those, such as the imino-compounds, which have the complex HC·C:NH, and leads to the

general conclusion that when the terminal hydrogen atoms in systems of this type are all replaced, the tendency for the compound to acquire that hydrogen atom which is necessary to enable it to react in its tautomeric form is such that any group capable of replacement by hydrogen is at once eliminated in the presence of a suitable reagent.

In the next communication several instances are recorded in which this reaction has been employed for the preparation of substituted glutaconic acids. These examples clearly prove that when the mobile hydrogen atoms in derivatives of glutaconic acid are replaced, the tendency for the compound to acquire the mobile atom causes it to eliminate one carboxyl group as ethyl carbonate when it is treated with alcoholic sodium ethoxide.

EXPERIMENTAL.

Ethyl Hydrindene-2:2-dicarboxylate,

$$C_6H_4{<}{CH_2 \atop CH_2}{>}C(CO_2Et)_2.$$

This substance was originally prepared by v. Baeyer and Perkin (*Ber.*, 1884, **17**, 122) by the condensation of *o*-xylylene dibromide and the sodium compound of ethyl malonate. It was, however, hydrolysed to the acid without further purification. The method of preparation used by us was the same as that employed by these chemists, but we find that the ester boils at 186°/19 mm., and that it sets to a crystalline mass on cooling. When recrystallised from a small quantity of alcohol it is obtained in long needles, which melt at 38°:

0·2030 gave 0·5092 CO_2 and 0·1272 H_2O. C = 68·81; H = 6·9.

$C_{16}H_{18}O_4$ requires C = 68·7; H = 6·9 per cent.

The ester is quite unaltered by sodium ethoxide.

Ethyl cyclo*Pentane-1:1:3:3-tetracarboxylate,*

$$\begin{matrix} CH_2\cdot C(CO_2Et)_2 \\ | \\ CH_2\cdot C(CO_2Et)_2 \end{matrix}{>}CH_2.$$

This substance was prepared by Pospischill's method (*Ber.*, 1898, **31**, 1950) from ethyl butanetetracarboxylate,

$$(CO_2Et)_2CH\cdot CH_2\cdot CH_2\cdot CH(CO_2Et)_2,$$

which was obtained both by the condensation of ethylene dibromide and ethyl sodiomalonate and by the condensation of ethyl cyclopropane-1:1-dicarboxylate, which is also formed in this action, with a further quantity of the sodium compound of ethyl malonate. The desired ester was obtained by condensing ethyl butanetetracarboxylate with methylene iodide. We find that it can be distilled

under 15 mm. pressure when small quantities are employed, and boils at 225—227°:

0·2013 gave 0·4201 CO_2 and 0·1342 H_2O. C=56·93; H=7·41.

$C_{17}H_{28}O_8$ requires C=57·0; H=7·3 per cent.

The ester was treated with two atomic proportions of sodium dissolved in alcohol, but was recovered unchanged.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXLVII.—*The Chemistry of the Glutaconic Acids. Part I. Methods for the Preparation of the Alkylglutaconic Acids which Prove the Identity of the α- and γ-Positions in the Glutaconic Acid Molecule.**

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

SOME years ago one of us, in conjunction with H. Rogerson (Trans., 1905, **87**, 1669, 1685), published a new method by which alkyl derivatives of glutaconic acid, having a methyl group in the β-position, and any desired alkyl group in either the α- or γ-position, or in both of these, could be prepared in quantity. The method involved the condensation of the sodium derivative of ethyl cyanoacetate with ethyl acetoacetate, when a reaction occurred which is expressed by the equation:

$$CO_2Et\cdot CHNa\cdot CN + HO\cdot CMe\colon CH\cdot CO_2Et \longrightarrow CO_2Et\cdot CNa(CN)\cdot CMe\colon CH\cdot CO_2Et + H_2O.$$

By heating this sodium derivative, or, better, the potassium compound, with alkyl iodides, the corresponding alkyl derivatives were produced, and these, when further treated with sodium ethoxide and an alkyl iodide, yielded the trialkylated esters, thus:

$$CO_2Et\cdot CR(CN)\cdot CMe\colon CNa\cdot CO_2Et + RI \longrightarrow CO_2Et\cdot CR(CN)\cdot CMe\colon CR\cdot CO_2Et.$$

An important feature of this reaction is that the hydrogen of the complex $\colon CH\cdot CO_2Et$, which is present in the dialkylated ester, is readily displaced by sodium. This is contrary to the conclusion arrived at by Blaise (*Bull. Soc. chim.*, 1903, [iii], **29**, 1016; *Compt. rend.*, 1903, **136**, 381, 692, 1140), who found that only those

* For the abstract of this paper see Proc., 1911, **27**, 122.

derivatives of glutaconic ester which contain the complex $\dot{:}C{\cdot}CHX{\cdot}$ react with sodium ethoxide. Now it is certain that compounds having this structure react in this manner, a fact which is clearly proved, not only by the work of Henrich (*Monatsh.*, 1899, **20**, 56) who discovered this reaction by preparing *aa*-dimethylglutaconic acid from the product of the methylation of ethyl glutaconate,

$$CO_2Et{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2Et \longrightarrow CO_2Et{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CO_2Et$$

but also by the subsequent work of Perkin and Smith (Trans., 1903, **83**, 8) and of Blaise (*loc. cit.*). It is, however, also certain that the property of this complex of yielding a sodium compound is entirely determined by the tendency of the mobile hydrogen atom present in the glutaconic acid derivative to pass outside the three-carbon system to the neighbouring carbonyl group. Thus the sodium compounds of this type are always yellow, and there is no doubt that they possess a structure represented by the expression $\cdot C{:}C{\cdot}C{:}C(ONa){\cdot}OEt$. Abundant proof will be given in this and in the subsequent papers of this series showing that the property of glutaconic acid derivatives of forming compounds of this type diminishes with the increase of alkyl groups in the molecule, and thus the trialkyl derivatives, $CN{\cdot}CHMe{\cdot}CMe{:}CMe{\cdot}CO_2Et$ and $CO_2Et{\cdot}CHMe{\cdot}CMe{:}CMe{\cdot}CO_2Et$, do not form sodium derivatives with sodium ethoxide (Trans., 1905, **87**, 1702, 1706). It has also been shown by Feist and Beyer (*Annalen*, 1906, **345**, 117) that the introduction of a methyl group into the ester $CO_2Et{\cdot}CHMe{\cdot}CMe{:}CH{\cdot}CO_2Et$ (or $CO_2Et{\cdot}CH_2{\cdot}CMe{:}CMe{\cdot}CO_2Et$) cannot be effected by the aid of sodium ethoxide and methyl iodide. It therefore follows that in the absence of the mobile hydrogen atom, and possibly, also, owing to the presence of negative groups on the more remote carbon atom, the hydrogen atom of the complex $\dot{:}CHX$ is displaceable by sodium, but such sodium compounds are without colour, and presumably have the metal attached to carbon.

The chief proof of the virtual tautomerism of the glutaconic acid molecule advanced in the former paper rested on the structure of two esters (I and II):

$$CO_2Et{\cdot}CMe(CN){\cdot}CMe{:}CH{\cdot}CO_2Et. \quad \text{(I.)}$$

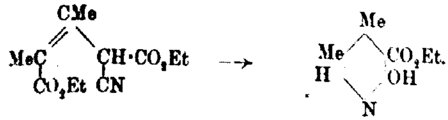
$$CO_2Et{\cdot}CH(CN){\cdot}CMe{:}CMe{\cdot}CO_2Et \quad \text{(II.)}$$

Ester (I) was prepared by the condensation of the potassium compound, to which we assigned the constitution

$$CO_2Et{\cdot}CK(CN){\cdot}CMe{:}CH{\cdot}CO_2Et,$$

with methyl iodide. Ester (II) was prepared by the condensation

of ethyl sodiocyanoacetate and ethyl methylacetoacetate. The structure of these two esters was shown to be different by the transformation of (II) into a derivative of dihydroxypyridine by the action of concentrated sulphuric acid, thus:



whereas (I) remained unacted on under the same experimental conditions.

From the fact that esters (I) and (II) yielded the same dimethylglutaconic acid on hydrolysis, it was concluded that the molecule of glutaconic acid is symmetrical, and that the α- and γ-positions in this substance are identical. It was also shown that β-methyl-α-ethylglutaconic acid, $CO_2H\cdot CHEt\cdot CMe{:}CH\cdot CO_2H$, and β-methyl-γ-ethylglutaconic acid, $CO_2H\cdot CEt{:}CMe\cdot CH_2\cdot CO_2H$, prepared by a similar method were also identical. Since that time the correctness of this conclusion has not been generally accepted, and it has been suggested (Meyer and Jacobson, "Lehrbuch der Organischen Chemie," 1910, 2te Aufl, I, ii, 440) that, during the process of the hydrolysis, the bond must have shifted in either one case or the other, thus yielding the same acid. This point was fully discussed at the time, but was discarded as highly improbable.

It is unfortunate that the real issue, namely, the identity of the α- and γ-positions, should have been masked in the previous paper by the mis-statement that only those derivatives of glutaconic acid which have the mobile hydrogen atom substituted can exist in two modifications. This error was quickly corrected by Feist (*Annalen*, 1906, **345**, 77), who pointed out that β-methylglutaconic acid, $CO_2H\cdot CH_2\cdot CMe{:}CH\cdot CO_2H$, had already been prepared in two well-defined modifications, a fact which had escaped our notice.

Since then, Feist (*Annalen*, 1909, **370**, 41) and Feist and Pomme (*ibid.*, 61) have shown that α-methylglutaconic acid,

$$CO_2H\cdot CHMe\cdot CH{:}CH\cdot CO_2H,$$

can be isolated in two modifications, but that the *cis*-form is relatively unstable. It is therefore evident that, if our view of the constitution of glutaconic acid is correct, the occurrence of stereoisomeric forms must be independent of the mobile hydrogen atom, and it therefore seemed to us desirable to institute a series of experiments on the chemistry of these substances. In the present paper we shall show:

(1) That the α-alkylglutaconic acids, $CO_2H\cdot CHR\cdot CH{:}CH\cdot CO_2H$,

and the γ-alkylglutaconic acids, $CO_2H\cdot CH_2\cdot CH{:}CR\cdot CO_2H$, are the same substances, and that α-methyl-γ-ethylglutaconic acid,

$$CO_2H\cdot CHMe\cdot CH{:}CEt\cdot CO_2H,$$

and γ-methyl-α-ethylglutaconic acid, $CO_2H\cdot CHEt\cdot CH{:}CMe\cdot CO_2H$ are identical.

(2) That the stability of the *cis*-forms of the α-substituted acids increases with the molecular weight of the substituting group.

It is probable that the cause of the identity of the α- and γ-positions is of the same order as that determining the equality of the meta-positions in the benzene ring, and in the ensuing papers we propose to write the formulæ of these substances thus:

$$CO_2H\cdot CH\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H,$$

indicating the mobile hydrogen atom by means of heavy type, but we have retained the older formulæ in the introduction for the sake of clearness.

At the same time it is necessary to offer some explanation respecting the cause of the existence of stereoisomerism among certain members of this series, because it is evident that the presence of the mobile hydrogen atom must prevent the occurrence of isomerism corresponding with maleic and fumaric acids. The explanation we suggest is as follows: The stereoisomerism of the acids of the type $CO_2H\cdot CR_2\cdot CH{:}CH\cdot CO_2H$, in which the mobile hydrogen atom is displaced, has been clearly established, and there is no doubt that this isomerism is represented by the formulæ.

$$\begin{array}{c} CO_2H\cdot CH \\ \| \\ CO_2H\cdot CR_2\cdot CH \end{array} \qquad \begin{array}{l} CO_2H\cdot CH \\ \qquad \| \\ \quad CH\cdot CR_2\cdot CO_2H \end{array}$$

cis-(Maleic)-form. *trans*-(Fumaric)-form.

Of the acids containing the mobile hydrogen atom, β-methylglutaconic acid, $CO_2H\cdot CH_2\cdot CMe{:}CH\cdot CO_2H$, exists in two well defined forms, and Feist has shown that α-methylglutaconic acid, $CO_2H\cdot CHMe\cdot CH{:}CH\cdot CO_2H$, can be isolated in a *cis*-modification melting at 118°, which is relatively unstable, and can only be formed from the anhydride in the presence of casein. In the present paper we show that *cis*-α-ethylglutaconic acid and *cis*-α-benzylglutaconic acid are stable substances. In spite of numerous attempts we have not yet succeeded in isolating any other of the "mobile" alkylglutaconic acids in two modifications, but we agree with Feist that such forms must be capable of existence, but are difficult to isolate owing to their instability. It is considered that the so-called stereoisomerism of these acids is in reality structural isomerism, and is a property depending on a difference in structure of the carboxyl groups. It is proposed to deal fully with this question in Part IV. of this series, but the terms

cis- and *trans-* are retained in this and the succeeding paper for the sake of clearness.

Preparation of the Alkylglutaconic Acids.

The preparation of alkyl derivatives of glutaconic acids having a methyl group in the β-position has already been described; the preparation in quantity of alkylglutaconic acids having this position unoccupied was a problem which had to be solved.

The α-substituted derivatives can be readily prepared by the alkylation of the yellow sodium compound which Conrad and Guthzeit (*Annalen*, 1883, **222**, 259) prepared by the action of chloroform on the sodium compound of ethyl malonate:

$$(CO_2Et)_2CNa\cdot CH{:}C(CO_2Et)_2 + RI \longrightarrow (CO_2Et)_2CR\cdot CH{:}C(CO_2Et)_2 + NaI;$$

but the preparation of further alkylated products is a matter of some difficulty. (For a description of these methods compare Feist, *Annalen*, 1909, **370**, 41).

We ultimately devised a method for the preparation of these acids which rests upon an observation recorded in the previous paper (Trans., 1905, **77**, 1702), namely, that ethyl α-cyano-$\alpha\beta\gamma$-trimethylglutaconate readily passes into ethyl carbonate and ethyl α-cyano-$\alpha\beta\gamma$-trimethylcrotonate when it is treated with cold sodium ethoxide, thus:

$$CO_2Et\cdot CMe(CN)\cdot CMe{:}CMe\cdot CO_2Et + EtOH \longrightarrow CHMe(CN)\cdot CMe{:}CMe\cdot CO_2Et + CO(OEt)_2.$$

This reaction suggested the general principle that when the mobile hydrogen atoms in compounds of the type of glutaconic ester are all displaced the tendency for the compound to acquire the hydrogen atom necessary for tautomerism is such that the element is at once introduced in the presence of a suitable reagent.

The alkyl derivatives prepared by the action of an alkyl iodide on Conrad and Guthzeit's yellow sodium compound are of this type, and should therefore react with cold sodium ethoxide, thus:

$$(CO_2Et)_2CR\cdot CH{:}C(CO_2Et)_2 + EtOH \longrightarrow CO_2Et\cdot CHR\cdot CH{:}C(CO_2Et)_2 + CO(OEt)_2.$$

Experiment showed that this reaction proceeded quantitatively, but that in the presence of sodium ethoxide the metal passed to the most negative carbon atom, yielding a sodium compound of the formula *:

$$CO_2Et\cdot CR{:}CH\cdot CNa(CO_2Et)_2.$$

* The sodium compounds, which are deep yellow, are written in this form for the sake of clearness, although they have undoubtedly the enolic formulæ assigned to them by Heurich (*Annalen*, 1910, **376**, 122).

This was proved by treating the sodium compound, when R = Me, with methyl iodide, when the product on hydrolysis yielded Reformatzky's αγ-dimethylglutaconic acid,

$$CO_2H\cdot CHMe\cdot CH{:}CMe\cdot CO_2H,$$

unaccompanied by any other acid.

The speed of the reaction varies with the value of R; thus when R = methyl the change from the tetraethyl to the triethyl ester is complete in the course of an hour at the ordinary temperature. When R = ethyl, two to two and a-half hours are required, and when R = benzyl the reaction takes at least twelve hours before the transformation is completely effected.

When the above sodium compound is treated with an alkyl iodide the ester $CO_2Et\cdot CR{:}CH\cdot CR(CO_2Et)_2$ is formed; this is another instance of a glutaconic ester in which the mobile hydrogen atoms are displaced.

It should therefore react with cold sodium ethoxide, thus:

$$CO_2Et\cdot CR{:}CH\cdot CR(CO_2Et)_2 + EtOH \longrightarrow$$
$$CO_2Et\cdot CR{:}CH\cdot CHR\cdot CO_2Et + CO(OEt)_2$$

This reaction also proceeds quantitatively, but here again the time varies with the value of R. It is not possible to eliminate more than one carbethoxy-group from an alkyl derivative of ethyl dicarbethoxyglutaconate or similarly constituted ethyl ester, even by using two equivalent proportions of sodium ethoxide; thus ethyl αγ-dicarbethoxy-α-methylglutaconate when left for several hours in contact with twice the quantity necessary to eliminate one carbethoxy-group yields only the triethyl ester, thus:

$$(CO_2Et)_2CMe\cdot CH{:}C(CO_2Et)_2 \longrightarrow CO_2Et\cdot CHMe\cdot CH{:}C(CO_2Et)_2$$

It is evident that this is caused by the production of the sodium compound, $CO_2Et\cdot CMe{:}CH\cdot C(CO_2Et){:}C(ONa)\cdot OEt$, and the elimination of a further carbethoxy-group from this substance would not supply the hydrogen atom necessary for virtual tautomerism.

It is therefore necessary in all these reactions to have one molecular proportion of sodium ethoxide present. If, however, the product does not form a sodium derivative, or forms a derivative which is dissociated by alcohol, then the change is effected by the aid of a trace of sodium ethoxide; thus the reaction:

$$CO_2Et\cdot CMe(CN)\cdot CMe{:}CMe\cdot CO_2Et + EtOH \longrightarrow$$
$$CHMe(CN)\cdot CMe{:}CMe\cdot CO_2Et + CO(OEt)_2$$

can be brought to completion in the presence of one-tenth the molecular quantity of sodium ethoxide. By this means, therefore, we had at our disposal a method by which any alkyl derivative of glutaconic acid substituted in either the α- or γ-positions or in both of them by any desired alkyl group could be prepared in

quantity, and we then proceeded to gain fresh evidence of the identity of the α- and γ-positions in the glutaconic acid molecule.

The Identity of α- and γ-Alkylglutaconic Acids.

α-Methylglutaconic acid is prepared by the hydrolysis of the ester $(CO_2Et)_2CMe\cdot CH\colon C(CO_2Et)_2$, and we satisfied ourselves that the same acid, unaccompanied by any other modification, was formed from this ester, both by acid and alkaline hydrolysis.

The action of sodium ethoxide on the ester produces, as already mentioned, a sodium compound of the formula

$$CO_2Et\cdot CMe\colon CH\cdot CNa(CO_2Et)_2,$$

and the ester prepared from this sodium derivative by the action of acids should on hydrolysis yield γ-methylglutaconic acid,

$$CO_2H\cdot CMe\colon CH\cdot CH_2\cdot CO_2H.$$

Both by acid and alkaline hydrolysis the ester yields the already known α-methylglutaconic acid unaccompanied by any other substance. In order to place the identity of these positions beyond question, we prepared the sodium compound:

$$CO_2Na\cdot CMe\colon CH\cdot CNa(CO_2Na)_2,$$

from which was obtained the already known methylglutaconic acid. It is clear, therefore, that α-methyl- and γ-methyl-glutaconic acids are the same substance. In the same way it was shown that both α- and γ-ethylglutaconic acids and α- and γ-benzylglutaconic acids, respectively, are identical.

The Identity of α-Methyl-γ-ethylglutaconic Acid and γ-Methyl-α-ethylglutaconic Acid.

γ-Methyl-α-ethylglutaconic acid, $CO_2H\cdot CMe\colon CH\cdot CHEt\cdot CO_2H$, was prepared by the following series of reactions: Ethyl $\alpha\gamma$-dicarbethoxy-α-methylglutaconate, $(CO_2Et)_2CMe\cdot CH\colon C(CO_2Et)_2$, was converted into the sodium compound, $CO_2Et\cdot CMe\colon CH\cdot CNa(CO_2Et)_2$, which on ethylation furnished the ethyl derivative,

$$CO_2Et\cdot CMe\colon CH\cdot CEt(CO_2Et)_2.$$

This ester was hydrolysed (1) through the sodium salt,

$$CO_2Na\cdot CMe\colon CH\cdot CEt(CO_2Na)_2,$$

and (2) through the compound $CO_2Et\cdot CMe\colon CH\cdot CHEt\cdot CO_2Et$ (see p. 2192). The methylethylglutaconic acid prepared by these two processes was the same substance; it must therefore be γ-methyl-α-ethylglutaconic acid, $CO_2H\cdot CMe\colon CH\cdot CHEt\cdot CO_2H$.

α-Methyl-γ-ethylglutaconic acid, $CO_2H\cdot CEt\colon CH\cdot CHMe\cdot CO_2H$, was prepared in the following way: The sodium derivative,

$$(CO_2Et)_2CNa\cdot CH\colon C(CO_2Et)_2,$$

on ethylation gave the ethyl compound,

$$(CO_2Et)_2CEt\cdot CH\colon C(CO_2Et)_2,$$

and this on treatment with sodium ethoxide yielded the so[dium] compound, $CO_2Et\cdot CEt\colon CH\cdot CNa(CO_2Et)_2$, which on methylation furnished the methyl compound, $CO_2Et\cdot CEt\colon CH\cdot CMe(CO_2Et)_2$.

As in the previous case, this ester was hydrolysed (1) through the sodium salt, $CO_2Na\cdot CEt\colon CH\cdot CMe(CO_2Na)_2$, and (2) through the compound $CO_2Et\cdot CEt\colon CH\cdot CHMe\cdot CO_2Et$ (see p. 2192). The same acid was produced by both these methods, and it must therefore be α-methyl-γ-ethylglutaconic acid,

$$CO_2H\cdot CEt\colon CH\cdot CHMe\cdot CO_2H.$$

γ-Methyl-α-ethylglutaconic acid and α-methyl-γ-ethylglutaconic acid prepared by these methods are the same compound.

During the course of these experiments it has been frequently noticed that the esters of substituted glutaconic acids tend to decompose during alkaline hydrolysis, yielding derivatives of malonic acid. A similar instance of this kind was recorded in a previous paper (Trans., 1905, **87**, 1693; compare also Claisen, *Annalen*, 1897, **297**, 89; Bolam, *Ber.*, 1894, **27**, 3061; Guthzeit and Bolam, *J. pr. Chem.*, 1896, [ii], **54**, 359), when it was found that ethyl α-cyano-β-methylglutaconate,

$$CO_2Et\cdot CH(CN)\cdot CMe\colon CH\cdot CO_2Et,$$

yielded some malonic acid when hydrolysed by alcoholic potassium hydroxide. In the present paper it is shown that the tendency for esters of this type to undergo fission appears to increase with the molecular weight of the groups present in the molecule; thus the ester $CO_2Et\cdot CHMe\cdot CH\colon C(CO_2Et)_2$ is hydrolysed completely to α-methylglutaconic acid, but, under the same conditions, the ester $CO_2Et\cdot CHEt\cdot CH\colon C(CO_2Et)_2$ yields a small quantity of ethylmalonic acid, whilst the ester $CO_2Et\cdot CH(CH_2Ph)\cdot CH\colon C(CO_2Et)_2$ yields benzylmalonic acid, the amount representing about 1[illegible] per cent. of the ester hydrolysed. This last reaction recalls the behaviour of benzaldehyde towards potassium hydroxide, and it is possible that the mechanism of these reactions involves the formation of the aldehyde, thus:

$$CO_2Et\cdot CHR\cdot CH\colon C(CO_2Et)_2 + H_2O \longrightarrow CO_2Et\cdot CHR\cdot CHO + CH_2(CO_2Et)_2.$$

It is significant that only those esters which contain a mobile hydrogen atom behave in this manner, and that the corresponding tetracarboxylic esters of the type $(CO_2Et)_2CR\cdot CH\colon C(CO_2Et)_2$ are hydrolysed directly to the acid without undergoing any disruption. It is of importance to remember this point when preparing the alkyl derivatives of glutaconic acid, because experiment shows that the best yield of acid is obtained from esters containing the mobile

hydrogen atom by hydrolysing them with acid hydrolysing agents, whereas the esters which have the mobile hydrogen atom displaced are best hydrolysed by alkaline hydroxides.

Guthzeit and Dressel have shown (*Ber.*, 1889, **22**, 1415) that when ethyl dicarbethoxyglutaconate is distilled under diminished pressure, alcohol is eliminated and ethyl 6-ethoxy-α-pyrone-3:5-dicarboxylate is formed, thus:

$$\begin{array}{lcl} CO_2Et\cdot CH\cdot CH{:}C(CO_2Et)_2 & \longrightarrow & CO_2Et\cdot C{:}CH\cdot C(CO_2Et){:}C\cdot OEt \\ \quad CO_2Et & & \quad CO_2Et \qquad\qquad\quad OH \\ & \longrightarrow & CO_2Et\cdot C{:}CH\cdot C(CO_2Et){:}C\cdot OEt \\ & & \qquad CO\text{———————}O \quad . \end{array}$$

The formation of a pyrone derivative in this manner shows that in a compound of the type of ethyl dicarbethoxyglutaconate there is a considerable tendency for the mobile hydrogen atom to pass outside the three-carbon system, and, as a matter of fact, it is probable that this ester, which gives a marked coloration with ferric chloride, consists largely of the enolic form at the ordinary temperature.

It is shown in this and the succeeding papers that the tendency for the mobile hydrogen atom to pass outside the three-carbon system is mainly determined by the nature of the groups attached to the α-carbon atom, and it is therefore of interest to compare the properties of the corresponding triethyl esters, which also contain the mobile hydrogen atom, as regards their capacity for forming pyrone derivatives; thus ethyl carbethoxy-α-methylglutaconate, $CO_2Et\cdot CHMe\cdot CH{:}C(CO_2Et)_2$, gives no coloration with ferric chloride, and can be distilled without undergoing change. Ethyl carbethoxy-α-ethylglutaconate, $CO_2Et\cdot CHEt\cdot CH{:}C(CO_2Et)_2$, also gives no coloration with ferric chloride, and is likewise unaltered on distillation. Ethyl carbethoxy-α-benzylglutaconate,

$$CO_2Et\cdot CH(CH_2Ph)\cdot CH{:}C(CO_2Et)_2,$$

on the other hand, gives a marked coloration with ferric chloride, and when slowly distilled passes into ethyl 6-ethoxy-3-benzyl-α-pyrone-5-carboxylate, thus:

$$\begin{array}{lcl} CH_2Ph\cdot CH\cdot CH{:}C(CO_2Et)_2 & \longrightarrow & CH_2Ph\cdot C{:}CH\cdot C(CO_2Et){:}C\cdot OEt \\ \quad CO_2Et & & \qquad CO_2Et \qquad\qquad OH \\ & \longrightarrow & CH_2Ph\cdot C{:}CH\cdot C(CO_2Et){:}C\cdot OEt \\ & & \qquad\quad CO\text{———————}O \quad . \end{array}$$

So far, this is the only triethyl ester of the series which we have succeeded in transforming into the pyrone ring, and it is evident that the presence of a large group attached to the α-carbon atom is necessary in order to displace the mobile hydrogen atom from

the three-carbon system. The dicarboxylic esters of the series are quite unaltered on distillation.

Experimental.

Ethyl $\alpha\gamma$-Dicarbethoxy-α-methylglutaconate, $(CO_2Et)_2CMe \cdot CH{:}C(CO_2Et)_2$.

The methylation of the yellow sodium compound of ethyl dicarbethoxyglutaconate was effected by Conrad and Guthzeit (*Annalen*, 1883, **222**, 259), who employed the action of alcoholic methyl iodide in sealed tubes at a high temperature for this purpose. Ruhemann (Trans., 1893, **63**, 880) found that the presence of alcohol led to unsatisfactory results, and therefore heated the yellow sodium compound to a high temperature with methyl iodide alone. Feist and Pomme (*Annalen*, 1909, **370**, 63), who succeeded in isolating the two stereoisomeric forms of α-methylglutaconic acid, prepared the acid of higher melting point by hydrolysing the above methyl derivative, which they prepared by the action of alcoholic methyl sulphate on the yellow sodium derivative.

The first two methods of preparation are tedious, and so far as the last-named process is concerned we were quite unable to reproduce the conditions given by Feist and Pomme in their paper. In our hands the action of methyl sulphate yielded hardly 10 per cent. of the methyl derivative, the remainder of the product comprising unaltered ethyl dicarbethoxyglutaconate,* together with ethyl 6-ethoxy-α-pyrone-3:5-dicarboxylate, melting at 94°, a substance which Guthzeit and Dressel (*Ber.*, 1889, **22**, 1415) have prepared previously. Ultimately we found that the best way to prepare ethyl dicarbethoxy-α-methylglutaconate is merely to heat a solution of the yellow sodium compound (50 grams) in alcohol (120 grams) with methyl iodide (30 grams) on the water-bath for five hours. The colourless solution was poured into water and extracted by ether; the ethereal extract, after being washed with water and shaken with a 10 per cent. solution of potassium hydroxide until the extract ceased to be yellow, was dried and evaporated. The residual oil yielded on distillation 40 grams of pure ethyl dicarbethoxy-α-methylglutaconate, boiling at 21?°/21 mm., that is, 83 per cent. of the theoretical amount. (Found: C=55·71; H=7·02. Calc., C=55·8; H=7·0 per cent.)

Hydrolysis.—Ten grams of the ethyl salt were boiled with dilute hydrochloric acid until completely hydrolysed, when the liquid was evaporated to a small bulk and allowed to crystallise. The acid

* The yellow colour of the sodium compound is entirely discharged in this experiment. The reaction is therefore complete.

is best prepared, however, by hydrolysis with an alcoholic solution containing one and a-half times the calculated quantity of potassium hydroxide, when the clear solution of the potassium salt, which evolves carbon dioxide on acidification, yields the pure acid on extraction by ether. Owing to the insolubility of α-methylglutaconic acid in dry ether, the acid separates in a very pure condition when the dried ethereal solution is evaporated to a small bulk. By both these methods the already known α-methylglutaconic acid melting at 145—146° was obtained, unaccompanied by any other substance. (Found, C=49·84; H=5·70. Calc., C=50·0; H=5·6 per cent.)

Ethyl Carbethoxy-α-methylglutaconate, $CO_2Et\cdot CMe\cdot CH(H)\cdot C(CO_2Et)_2$.

The elimination of one carbethoxy-group from ethyl dicarbethoxy-α-methylglutaconate was effected as follows: Forty grams of the tetraethyl ester dissolved in 30 c.c. of alcohol were mixed with a solution containing 2·8 grams of sodium in 32 c.c. of alcohol. The solution became warm and deep yellow, whilst the characteristic odour, which always accompanies the production of ethyl carbonate in these reactions, was at once apparent. After an hour the mixture was poured into dilute hydrochloric acid, and the oil extracted by ether. The ethereal extract after being washed was shaken with a little dilute alkali, dried, and evaporated. The residual oil was then distilled under ordinary pressure until the thermometer registered 140°, when the operation was continued under diminished pressure. The triethyl ester distilled at 182°/[illegible] mm. as a colourless oil without appreciable odour. Yield, [illegible] grams, or 93 per cent. of the theoretical:

0·2311 gave 0·4838 CO_2 and 0·1505 H_2O. C=57·10; H=7·25.

$C_{13}H_{20}O_6$ requires C=57·3; H=7·4 per cent.

The substance gives no colour with ferric chloride.

The less volatile portion was fractionated under the ordinary pressure, and the large fraction, which boiled at 126°, was characterised as ethyl carbonate by analysis. (Found, C=50·58; H=8·50. Calc., C=50·8; H=8·5 per cent.)

α(or γ)-*Methylglutaconic Acid*, $CO_2H\cdot CMe\cdot CH(H)\cdot CH\cdot CO_2H$.

Ethyl carbethoxy-α-methylglutaconate was subjected to the hydrolysing action of both acids and alkalis in order to prove that α- and γ-methylglutaconic acids were the same substance (compare p. 2193).

Acid Hydrolysis.—The ester was boiled with ten times its bulk of 10 per cent. hydrochloric acid until all had passed into solution, when the product was evaporated to half its volume, and the acid allowed to crystallise. The crude acid melted at 143—146°, and when recrystallised from water melted at 145—146°. The filtrate from the crude acid gave on evaporation an acid which melted at 142—144°, and it is therefore evident that no other substance is formed during the hydrolysis. The acid was proved to be the already known α-methylglutaconic acid by direct comparison with the acid prepared as described on p. 2197.

Alkaline Hydrolysis: Formation of the Sodium Salt, $CO_2Na{\cdot}CMe{:}CH{\cdot}CNa(CO_2Na)_2$.

—Twenty-six grams of the ester were added to a solution containing 8·4 grams of sodium dissolved in alcohol, to which 25 c.c. of water had been added. The whole was then warmed on the water-bath, when the yellow solution gradually deposited a white precipitate of the sodium salt. This was collected and washed with alcohol until quite colourless, when it was spread on a porous plate and dried at 80°:

0·4137 gave 0·4443 Na_2SO_4. Na = 33·15.

$C_7H_4O_8Na_4$ requires Na = 33·3 per cent.

The sodium salt was dissolved in ice-cold water, and cautiously acidified by the addition of the calculated quantity of hydrochloric acid. The strongly alkaline solution which the salt forms with water effervesced freely on the addition of the acid, and when all carbon dioxide had been evolved the solution was extracted by ether. The dried ethereal solution when evaporated yielded a solid acid, which melted at 133—140°. This was then rubbed with dry ether, in which it was very sparingly soluble, and yielded an acid melting at 145—146°. The identity of this acid with α-methylglutaconic acid was proved (1) by a mixed melting-point determination, (2) by the formation of the characteristic chloro-anhydride (see Part II). (Found, C = 49·88; H = 5·68. Calc., C = 50·0; H = 5·6 per cent.).

The small quantity of acid which remained on evaporating the ethereal washings from the purification of the above acid melted at 125—133°; when rubbed with a little dry ether this yielded a further quantity of the acid, melting at 145—146°. The ultimate residue, which did not weigh more than 0·5 gram, remained viscid even after some weeks. It possibly contained some of Feist's *cis*-modification melting at 118°, but we were unable to isolate any pure substance from it.

Ethyl αγ-Dicarbethoxy-α-ethylglutaconate, $(CO_2Et)_2CEt{\cdot}CH{:}C(CO_2Et)_2$.

As in the case of the corresponding methyl derivative, we found that by far the best way to prepare this compound is to heat an alcoholic solution of the yellow sodium compound together with excess of ethyl iodide on the water-bath for twenty-four hours. The product was worked up as described for the methyl derivative (p. 2197). The oil obtained boiled at 213°/20 mm.; yield, 80 per cent. of the theoretical. (Found, C=56·89; H=7·06. Calc., C=57·0; H=7·3 per cent.)

Ethyl Carbethoxy-α-ethylglutaconate, $CO_2Et{\cdot}CEt{\cdot}CH(H){\cdot}C(CO_2Et)_2$.

This substance was prepared by the action of cold alcoholic sodium ethoxide on ethyl dicarbethoxy-α-ethylglutaconate, but the reaction requires a longer time than is the case with the corresponding methyl derivative.

Thirty-one grams of the ethyl salt dissolved in 25 c.c. of alcohol were added to a solution containing 2 grams of sodium dissolved in 25 c.c. of alcohol. The mixture became warm and deep yellow, but the heat developed was not so great as with the methyl derivative. After three hours at the ordinary temperature the mixture was poured into dilute hydrochloric acid, and the oil extracted by ether. The residual liquid was then fractionated, and the fraction boiling at 180°/20 mm. collected. Yield, 95 per cent. of the theoretical:

0·2416 gave 0·5170 CO_2 and 0·1649 H_2O. C=58·36; H=7·60.
$C_{14}H_{22}O_6$ requires C=58·7; H=7·0 per cent.

Ethyl Carbethoxy-α-ethylglutaconate is a moderately viscid, colourless liquid without appreciable odour, and does not give a colour with ferric chloride. It was not thought necessary, in this case, to collect the ethyl carbonate formed in the reaction, but its presence was obvious, both from the odour and from the large quantity of material of low boiling point present.

α(or γ)-*Ethylglutaconic Acid,* $CO_2H{\cdot}CEt{\cdot}CH(H){\cdot}CH{\cdot}CO_2H$.

In the first instance we repeated the work of Guthzeit and Dressel (*Ber.*, 1890, **23**, 3182) on the preparation of this acid from ethyl dicarbethoxy-α-ethylglutaconate in order to satisfy ourselves that the same substance was produced by both acid and alkaline hydrolysis. This we found to be the case, but the melting point

of the acid (118—120°) given by the above chemists is much too low; the acid when pure melts at 133—134°.

From Ethyl Carbethoxy-α-ethylglutaconate: Acid Hydrolysis.—The method was the same as that employed in the preparation of α-methylglutaconic acid. The crude acid melted at 128—131°, and when recrystallised from water melted at 133—134°. Some ethylmalonic acid (m. p. 112°) was found in the mother liquor from the hydrolysis. (Found, C=45·2; H=6·08. Calc., C=45·5; H=6·1 per cent.)

Alkaline Hydrolysis.—The process was the same as with α-methylglutaconic acid, and the sodium salt, $CO_2Na\cdot CEt\colon CH\cdot CNa(CO_2Na)_2$, was obtained. The salt when dissolved in water and acidified with hydrochloric acid yielded on extraction with ether an acid melting at 128—130°, which after recrystallisation from water melted at 133—134°:

0·2294 gave 0·4476 CO_2 and 0·1294 H_2O. C=53·22; H=6·2.
$C_7H_{10}O_4$ requires C=53·2; H=6·3 per cent.

This form of α-ethylglutaconic acid evidently represents the *trans*-modification corresponding with *trans*-α-methylglutaconic acid melting at 145—146°. An acid of lower melting point which is prepared by the action of potassium hydroxide on the chloroanhydride of the acid will be described in Part II. of this series.

Ethyl αγ-Dicarbethoxy-α-benzylglutaconate,
$(CO_2Et)_2C(CH_2Ph)\cdot CH\colon C(CO_2Et)_2$.

The preparation of this substance was carried out in the same manner as that employed for the production of the alkyl derivatives already described. The oil boiled at 253°/18 mm., and set to a solid mass on cooling. The melting point of this ester (78°) showed it to be the same substance as prepared by Ruhemann (Trans. 1893, **63**, 259) and by Conrad and Guthzeit (*Annalen*, 1883, **222**, 261).

Ethyl γ-Carbethoxy-α-benzylglutaconate,
$CO_2Et\cdot C(CH_2Ph)\cdot CH(H)\cdot C(CO_2Et)_2$.

Thirty-five grams of ethyl dicarbethoxy-α-benzylglutaconate were dissolved in an equal volume of alcohol and mixed with a solution containing 1·9 grams of sodium dissolved in 25 c.c. of alcohol. The solution, which became deep orange and slightly warm, was kept at the ordinary temperature for twelve hours, when it was poured into dilute hydrochloric acid and the oil extracted by ether. The ethereal extract was then purified in the usual manner, and the oil which remained on evaporation distilled under diminished pressure. Ethyl carbonate, recognisable by its odour, passed over

first, but was not collected; the triethyl ester then distilled as a colourless, fairly viscid liquid at 218°/22 mm.:

0·2292 gave 0·5494 CO_2 and 0·1448 H_2O. C = 65·37; H = 7·02.

$C_{12}H_{24}O_6$ requires C = 65·5; H = 6·9 per cent.

An alcoholic solution of ethyl carbethoxy-α-benzylglutaconate gives a reddish-brown colour with ferric chloride.

Ethyl 6-Ethoxy-3-benzyl-α-pyrone-5-carboxylate,

$$\begin{array}{l} CH_2Ph\cdot C\!:\!CH\cdot C(CO_2Et)\!:\!C\cdot OEt \\ CO\text{———————}O \end{array}$$

There is always a quantity of material of higher boiling point formed in this reaction, and its presence is evidently caused by the decomposition of ethyl carbethoxy-α-benzylglutaconate during distillation, as when the pure triethyl ester is again distilled a further quantity of the fraction of higher boiling point is obtained. The pure decomposition product boils at 261°/25 mm., and sets to a crystalline mass on cooling. It crystallises from dilute alcohol in voluminous needles melting at 70°:

0·2044 gave 0·5044 CO_2 and 0·1095 H_2O. C = 67·35; H = 5·97.

$C_{17}H_{18}O_5$ requires C = 67·6; H = 6·0 per cent.

The ester yields α-benzylglutaconate acid on alkaline hydrolysis.

α- (or γ)-*Benzylglutaconic Acid*, $CO_2H\cdot C(CH_2Ph)\cdot CH(H)\cdot CH\cdot CO_2H$.

This acid is the sole product formed by the hydrolysis of ethyl carbethoxy-α-benzylglutaconate by either hydrochloric acid or alcoholic potassium hydroxide. It crystallises from water in clusters of needles melting at 153—154°. (Found, C = 65·40; H = 5·60. Calc., C = 65·5; H = 5·5 per cent.) In order to show the identity of the α- and γ-positions, the same process was adopted as with the α-methyl and α-ethyl acids. In this case, however, the quantity of sodium salt precipitated by the action of alcoholic sodium ethoxide containing a little water was much smaller than would be caused by the conversion of the ester into the sodium salt. When this salt was dissolved in water and acidified, a soluble acid was extracted by ether, which when recrystallised from an equal volume of concentrated hydrochloric acid and water melted at 120°, and was proved to be benzylmalonic acid. (Found, C = 61·67; H = 5·06. Calc., C = 61·9; H = 5·2 per cent. *Silver salt*: Found, Ag = 53·0. Calc., Ag = 53·0 per cent.)

The filtrate from the sodium salt yielded benzylglutaconic acid melting at 153—154°. This acid is probably the *trans*-modification of α-benzylglutaconate acid, as there is an acid of lower melting point which can be prepared from the chloro-anhydride by the action of potassium hydroxide. This substance, which is evidently

the *cis*-modification, crystallises from water in small plates, melting at 139°.

A full description of the preparation and properties of these substances will be found in Part II.

Ethyl Carbethoxy-αγ-dimethylglutaconate,

$CO_2Et{\cdot}CMe{:}CH{\cdot}CMe(CO_2Et)_2$.

This substance was usually prepared by treating the alcoholic solution of the sodium compound formed as described on p. 2197 with 20 per cent. excess of methyl iodide, and warming on the water-bath until the yellow colour of the solution was discharged. The product was then poured into water, and the oil extracted by ether. It was soon evident that the large quantity of methyl iodide used in the experiment had caused a partial conversion of the triethyl ester, and it was found possible by working with large quantities and isolating the first and last runnings from the distillation to obtain the triethyl and methyl diethyl esters in a condition sufficiently pure for analysis. It is, of course, well known that interchange of alkyloxy-groups frequently occurs in reactions of this type, but as it was necessary for our purpose to establish the constitution of our product, we thought it desirable, in one instance, to isolate the two esters and to hydrolyse them separately. With this object in view, 109 grams of ethyl dicarbethoxy-α-methylglutaconate were mixed with 60 c.c. of alcohol, and treated with a solution containing 7·3 grams of sodium dissolved in 90 c.c. of alcohol. After an hour 55 grams of methyl iodide were added and the solution was heated on the water-bath until the yellow colour had disappeared. Water was then added, and the ethyl ester isolated in the usual way.

Methyl Diethyl Carbethoxy-αγ-dimethylglutaconate.—As soon as all ethyl carbonate had distilled over, the temperature remained constant at 175°/20 mm., and the small fraction collected at this temperature was analysed:

0·2243 gave 0·4719 CO_2 and 0·1519 H_2O. C=57·42; H=7·51.

$C_{13}H_{20}O_6$ requires C=57·4; H=7·4 per cent.

Ethyl Carbethoxy-αγ-dimethylglutaconate.—The temperature then rose slowly, while the greater portion of the ester distilled over. It finally remained constant at 178°/20 mm., and the small fraction distilling at this temperature was analysed:

0·2397 gave 0·5167 CO_2 and 0·1656 H_2O. C=58·78; H=7·67.

$C_{14}H_{22}O_6$ requires C=58·7; H=7·7 per cent.

The two esters were hydrolysed separately by means of dilute hydrochloric acid, and as in each case αγ-dimethylglutaconic acid

as obtained as sole product, it is evident that they have the ...ructures assigned to them above.

In the other cases of this kind which occur in this paper it was ...t thought necessary to isolate the two ethyl esters, and the last ...nstant fraction was always analysed, unless stated otherwise.

Ethyl αγ-Dimethylglutaconate, $CO_2Et{\cdot}CMe{\cdot}CH(H){\cdot}CMe{\cdot}CO_2Et$.

The conversion of ethyl carbethoxy-αγ-dimethylglutaconate into ethyl carbonate and the above ester was effected in the following way. Sixty-one grams of the triethyl ester were mixed with 40 c.c. of alcohol, and treated with a cold solution of 4·9 grams of sodium in 60 c.c. of alcohol. The mixture turned yellow after a few seconds, and then became slightly warm; it was kept at the ordinary temperature for one and a-quarter hours, when it was poured into water and extracted by ether without acidifying. The oil obtained on evaporating the dried ethereal solution was distilled under the ordinary pressure until the thermometer registered 135°, when the oil remaining was distilled under diminished pressure. The whole amount distilled between 174—176°/81 mm., and the ...st runnings, constituting the above ester, were analysed:

0·2265 gave 0·4979 CO_2 and 0·1647 H_2O. C = 59·95; H = 8·10.

$C_{10}H_{16}O_4$ requires C = 60·0; H = 8·0 per cent.

The large fraction obtained by distilling under ordinary pressure as described above was again distilled, and the fraction boiling at ...° was shown to be ethyl carbonate. (Found, C = 50·70; H = 8·36. ...lc., C = 50·9; H = 8·5 per cent.)

The above conversion under the experimental conditions ...scribed was practically quantitative. When it is desired to ...repare αγ-dimethylglutaconic acid in quantity, it is always ...dvisable to hydrolyse the dialkyl rather than the triethyl ester. ...t was found that the tertiary esters of the type

$$CO_2R{\cdot}CMe{:}CH{\cdot}CMe(CO_2R)_2,$$

...re only very slowly hydrolysed by dilute hydrochloric acid, whereas ...he "mobile" ethyl esters, $CO_2R{\cdot}CMe{\cdot}CH(H){\cdot}CMe{\cdot}CO_2R$, are ...apidly converted into the acid under the same conditions.

αγ-Dimethylglutaconic Acid, $CO_2H{\cdot}CMe{\cdot}CH(H){\cdot}CMe{\cdot}CO_2H$.

This acid is obtained in a yield of 90 per cent. of the theory ...hen the dialkyl ester is boiled with ten times its volume of 10 per ...ent. hydrochloric acid until all oil has passed into solution. The ...eater proportion of the acid separates when the clear hydrochloric ...id solution is cooled, and a further quantity is obtained on ...aporating the filtrate to a small bulk.

Forty grams of the dialkyl ester gave in this way 23 grams of acid melting at 145—147°, which separated directly from the hydrochloric acid solution; a further 3 grams, melting at 137—142°, were obtained on evaporating the filtrate. Both products when recrystallised once from dilute hydrochloric acid gave pure αγ-dimethylglutaconic acid, melting at 147°. (Found, C = 53·2; H = 6·28. Calc., C = 53·2; H = 6·3 per cent.)

The constitution of this acid was proved, both by the formation of methylmalonic acid from it on oxidation with alkaline permanganate and by direct comparison with a specimen of αγ-dimethylglutaconic acid prepared by Reformatzky's method from ethyl β-hydroxy-αγ-dimethylglutarate,

$$CO_2H{\cdot}CHMe{\cdot}CH(OH){\cdot}CHMe{\cdot}CO_2H,$$

which was kindly sent us by Professor Feist.

The *silver* salt is a curdy, white precipitate:

0·4055 gave 0·2338 Ag. Ag = 57·74.

$C_7H_8O_4Ag_2$ requires Ag = 58·0 per cent.

Ethyl Carbethoxy-γ-methyl-α-ethylglutaconate, $CO_2Et{\cdot}CMe{:}CH{\cdot}CEt(CO_2Et)_2$.

This ester may be prepared by treating the sodium derivative obtained by the action of sodium ethoxide on ethyl dicarbethoxy-α-methylglutaconate as described on p. 2197 with ethyl iodide. Forty grams of ethyl dicarboxy-α-methylglutaconate were mixed with 30 grams of alcohol, and a solution containing 3 grams of sodium dissolved in 40 c.c. of alcohol were added. After the mixture had been kept at the ordinary temperature for one hour, 30 grams of ethyl iodide were added, and the solution was heated on the water bath for twelve hours. The pale yellow solution was then poured into water, and the ester isolated in the usual way. The oil when fractionated yielded the usual amount of ethyl carbonate and a constant fraction boiling at 180°/20 mm. Yield, 80 per cent. of the theoretical:

0·2018 gave 0·4427 CO_2 and 0·1487 H_2O. C = 59·83; H = 8·19.

$C_{15}H_{24}O_6$ requires C = 60·0; H = 8·0 per cent.

The fractionation has, however, to be carefully conducted, because a small quantity of the diethyl ester is also formed in the reaction. This secondary change is evidently due to the partial dissociation of the sodium compound in solution.

Ethyl α-Methyl-γ-ethylglutaconate, $CO_2Et{\cdot}CMe{\cdot}CH(H){\cdot}CEt{\cdot}CO_2Et_2$.

The transformation of ethyl carbethoxy-γ-methyl-α-ethylglutaconate into ethyl carbonate and the above ester was effected in the usual manner: Twenty grams of the ester were dissolved in 10 c.c. of alcohol, and mixed with a solution containing 1·6 grams of sodium dissolved in 20 c.c. of alcohol. The solution, which slowly became yellow and developed a slight amount of heat, was kept at the ordinary temperature for two hours, and then worked up as usual. The oil obtained distilled at 163°/23 mm.:

0·2177 gave 0·5027 CO_2 and 0·1746 H_2O. C = 62·96; H = 8·91.
$C_{12}H_{20}O_4$ requires C = 63·1; H = 8·8 per cent.

The yield of the diethyl ester by this process is almost quantitative. The ethyl carbonate formed in the reaction was refractionated under ordinary pressure, and the large fraction boiling at 126° was collected. (Found, C = 50·71; H = 8·59. Calc., C = 50·8; H = 8·5 per cent.)

Ethyl Carbethoxy-α-methyl-γ-ethylglutaconate, $CO_2Et{\cdot}CEt{:}CH{\cdot}CMe(CO_2Et)_2$.

The preparation of this substance from ethyl dicarbethoxyethylglutaconate (see p. 2199) was effected in the following manner: Sixty-two grams of the ester were mixed with 40 c.c. of alcohol, and a solution containing 4 grams of sodium dissolved in 50 c.c. of alcohol was added. After three hours at the ordinary temperature, 30 grams of methyl iodide were added, and the mixture heated on the water-bath for eight hours, by which time the strong yellow colour of the liquid had almost disappeared. The product was then poured into water, and the oil isolated in the usual manner. After the ethyl carbonate had been removed by distillation under ordinary pressure, the residue was fractionated under diminished pressure, and the small fraction boiling at 159°/23 mm. was collected:

0·2347 gave 0·5078 CO_2 and 0·1654 H_2O. C = 59·01; H = 7·82.
$C_{14}H_{22}O_6$ requires C = 58·7; H = 7·7 per cent.

This is therefore the methyl diethyl ester formed as explained on p. 2202. The main bulk of the product distilled between 180° and 183°, the yield of methyl diethyl and triethyl esters representing about 80 per cent. of the theoretical amount.

Ethyl α-Methyl-γ-ethylglutaconate, $CO_2Et\cdot CMe\cdot CH(H)\cdot CEt\cdot CO_2Et$

Although we have no direct evidence that the ethyl esters prepared by the elimination of a carbethoxyl group from ethyl carbethoxy-γ-methyl-α-ethylglutaconate and ethyl carbethoxy-α-methyl-γ-ethylglutaconate respectively are the same substance, excepting that they yield the same acid on hydrolysis, yet from the identity of the corresponding acids which we have established in this communication it would be unreasonable to suppose that the ethyl esters of the acids can be different compounds. We have therefore given to the above ethyl ester the same name and formula as that assigned to the ester described on p. 2205. The diethyl ester is prepared from ethyl carbethoxy-α-methyl-γ-ethylglutaconate as follows: Thirty grams of the mixed esters prepared as described above were dissolved in 15 c.c. of alcohol, and treated with a solution containing 2·3 grams of sodium dissolved in 30 c.c. of alcohol. The mixture was kept for three hours at the ordinary temperature, when it was poured into water and extracted by ether without acidifying. After the ethereal solution had been purified in the usual manner, the residual oil was distilled free from ethyl carbonate under ordinary pressure, and the remainder fractionated under diminished pressure. A small portion which distilled first at 160°/21 mm. was analysed:

0·2111 gave 0·4782 CO_2 and 0·1573 H_2O. C = 61·77; H = 8·30.

$C_{11}H_{18}O_4$ requires C = 61·7; H = 8·4 per cent.

The liquid was therefore the methyl ethyl ester. The main bulk of the product distilled at 160—163°/21 mm., the yield of the mixed esters being practically quantitative.

The ethyl carbonate formed in the reaction was obtained by refractionating the material of low boiling point, the portion boiling at 126° being analysed. (Found, C = 50·70; H = 8·45. Calc. C = 50·0; H = 8·5 per cent.)

α-Methyl-γ-ethylglutaconic Acid, $CO_2H\cdot CMe\cdot CH(H)\cdot CEt\cdot CO_2H$

For the sake of convenience we have placed all the experiments relating to this acid under one heading, but in order to show the identity of α-methyl-γ-ethylglutaconic acid and γ-methyl-α-ethylglutaconic acid it was necessary to prepare it by four different processes:

(1) *From Ethyl Carbethoxy-γ-methyl-α-ethylglutaconate by Alkaline Hydrolysis.*—Ten grams of the ester were added to an alcoholic solution containing 2·3 grams of sodium in 40 c.c. of alcohol, to which 5 c.c. of water had been added. A gelatinous

sodium salt slowly separated when the solution was warmed on the water-bath, and was collected. The salt was then thoroughly mixed with cold alcohol and again collected, this process being repeated three times. The salt still retained its gelatinous nature, but in spite of that was quite easy to filter; it was spread on a porous plate, and dried at 80°, when it was obtained as a fine, white powder:

0·3143 gave 0·2358 Na_2SO_4. Na = 24·31.

$C_9H_9O_6Na_3$ requires Na = 24·5 per cent.

This substance was therefore the sodium salt,

$CO_2Na{\cdot}CMe{:}CH{\cdot}CEt(CO_2Na)_2$.

The Acid from the Sodium Salt.—The salt was dissolved in a little ice-cold water, and the clear solution cautiously acidified by the addition of the calculated quantity of hydrochloric acid, when a vigorous evolution of carbon dioxide ensued. The solution, which had become turbid owing to the separation of the acid as an oil, was extracted by ether, and the ethereal extract dried and evaporated. The residual gum was then dissolved in a little water, and the acid allowed to crystallise. It melted at 114—115°, and after being recrystallised from water, at 116°.

(2) *From Ethyl γ-Methyl-α-ethylglutaconate by Acid Hydrolysis.* Ten grams of the ester were mixed with ten times its volume of 10 per cent. hydrochloric acid, and heated on the sand-bath until all oil had passed into solution. The acid separated as a gum when the hydrochloric acid solution was cooled, but when the liquid was scratched with a crystal of the acid obtained in the previous experiment while still warm, the acid separated in the crystalline condition. The crude product melted at 113—115°, and, after being recrystallised from water, at 116°. The identity of this acid with that obtained in the first experiment was established by direct comparison:

0·2105 gave 0·4297 CO_2 and 0·1366 H_2O. C = 55·67; H = 7·22.

$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

(3) *From Ethyl Carbethoxy-α-methyl-γ-ethylglutaconate by Alkaline Hydrolysis.*—The conditions of this experiment were essentially the same as those described in experiment (1), and a similar salt was obtained:

0·3040 gave 0·2289 Na_2SO_4. Na = 24·39.

$C_9H_9O_6Na_3$ requires Na = 24·5 per cent.

This substance was therefore the sodium salt,

$CO_2Na{\cdot}CEt{:}CH{:}CMe(CO_2Na)_2$.

Conversion into the Acid.—The salt was dissolved in a little ice-cold water, and the clear solution cautiously acidified by the

addition of the calculated quantity of hydrochloric acid. A vigorous evolution of carbon dioxide took place, and the solution became turbid owing to the separation of the acid, which melted at 115°, after having been once recrystallised from water.

(4) *From Ethyl α-Methyl-γ-ethylglutaconate by Acid Hydrolysis.* —The same conditions as in experiment (2) were observed, and an acid melting at 116° was obtained. A direct comparison of this acid with that obtained in experiment (3) showed them to be the same substance:

0·2336 gave 0·4788 CO_2 and 0·1456 H_2O. C=55·89; H=6·9;

$C_8H_{12}O_4$ requires C=55·8; H=7·0 per cent.

The identity of the four acids obtained by the processes was established by the mixed melting-point method, and by the conversion of each product into the hydroxy-anil described below. The acid crystallises from benzene in small needles; the crystals from water are not well defined.

The Hydroxy-anil of α-Methyl-γ-ethylglutaconic Acid.—A description of the aniline derivatives of α-methyl-γ-ethylglutaconic acid will be given in a future communication, but it is necessary here to give a brief account of the preparation of this anil, as its production was used as a means of identifying the acids prepared by the methods given above. It is formed when the acid is boiled with excess of aniline for two hours, and can be isolated by pouring the product into dilute hydrochloric acid, extracting the insoluble oil by means of ether, and shaking the ethereal solution with aqueous sodium carbonate. The oil which separates when the alkaline washings are acidified slowly becomes solid, and crystallises from dilute alcohol in long needles, melting at 92°.

THE SORBY RESEARCH LABORATORY,
THE UNIVERSITY, SHEFFIELD.

CCXLVIII.—*The Chemistry of the Glutaconic Acids. Part II. The Reactions of the Alkylglutaconic Acids Having one Mobile Hydrogen Atom.*

By FERDINAND BERNARD THOLE and JOCELYN FIELD THORPE.

FOR the purposes of the present papers we have divided the acids of the glutaconic acid series into three classes, namely:

Class I.—Containing those alkyl derivatives in which there is no mobile hydrogen atom, or, in other words, those compounds in which both hydrogen atoms attached to the α-carbon atom are

eplaced. A typical member of this class is αα-dimethylglutaconic cid, $CO_2H{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CO_2H$.

Class II.—Containing those alkyl derivatives in which there is ne mobile hydrogen atom, that is to say, those in which one ydrogen atom of the methylene group is displaced by an alkyl adicle, as in α-methylglutaconic acid, $CO_2H{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2H$, r, as we prefer to write the formula, $CO_2H{\cdot}CMe{\cdot}CH(H){\cdot}CH{\cdot}CO_2H$.

Class III.—Containing those compounds in which both hydrogen toms of the methylene group are free, as in glutaconic acid itself, nd the β-monoalkyl derivatives, such as β-methylglutaconic acid, $O_2H{\cdot}CH_2{\cdot}CMe{:}CH{\cdot}CO_2H$ or $CO_2H{\cdot}CH{\cdot}CMe(H){\cdot}CH{\cdot}CO_2H$.

As regards a compound falling within class I, the fixing of the ouble bond causes it to exhibit all the properties of a maleic or umaric acid, and to exist in well-defined *cis-* and *trans-*modifications, which may be represented by the formulæ:

$$\begin{array}{c} CO_2H{\cdot}CR_2{\cdot}CH \\ \| \\ CO_2H{\cdot}CH \\ \textit{cis-}. \end{array} \qquad\qquad \begin{array}{c} CH{\cdot}CR_2{\cdot}CO_2H \\ \| \\ CO_2H{\cdot}CH \\ \textit{trans-}. \end{array}$$

The known acids of this class may be summarised as follows:

	trans-.	*cis-*.	Anhydride.	Semi-anilide
αα-Dimethylglutaconic acid,* $CO_2H{\cdot}CMe_2{\cdot}CH{:}CH{\cdot}CO_2H$	172°	134—135	liquid	164°
ααβ-Trimethylglutaconic acid,† $CO_2H{\cdot}CMe_2{\cdot}CMe{:}CH{\cdot}CO_2H$	148	133	107°	138
ααγ-Trimethylglutaconic acid,‡ $CO_2H{\cdot}CMe_2{\cdot}CH{:}CMe{\cdot}CO_2H$	150	125	88	—

* Perkin and Smith (Trans., 1903, **83**, 8); Henrich (*Monatsh.*, 1899, **20**, 560); erkin (Trans., 1902, **81**, 253); Blaise (*Compt. rend.*, 1903, **136**, 381, 692).

† Perkin and Thorpe (Trans., 1897, **71**, 1182); Perkin and Smith (Trans., 1903, **83**, 774).

‡ Perkin and Smith (Trans., 1903, **83**, 771; 1904, **85**, 155).

So far, therefore, as the reactions of the mobile hydrogen atom are concerned, these compounds are without interest, as their reactions are in all respects normal. It is only with the members of classes II and III that the remarkable properties which we shall show are associated with the presence of the mobile hydrogen atom are in evidence; it is therefore with some of the acids of class II that we propose to deal in the present section, reserving a description of other acids for subsequent parts of this series.

It is apparent that the acids falling within class II may be of three types: (*a*) the monosubstituted derivatives, as α-methylglutaconic acid, $CO_2H{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2H$; (*b*) the disubstituted derivatives, such as αβ-dimethylglutaconic acid,

$$CO_2H{\cdot}CHMe{\cdot}CMe{:}CH{\cdot}CO_2H,$$

and αγ-dimethylglutaconic acid, $CO_2H{\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CO_2H$; and

(*c*) the trisubstituted derivatives, such as **$\alpha\beta\gamma$-trimethylglutaconic acid**, $CO_2H{\cdot}CHMe{\cdot}CMe{:}CMe{\cdot}CO_2H$. In the present paper we propose to deal with these derivatives in the above order.

(*a*) *The Monosubstituted Derivatives.*—The known acids of this type may be summarised as follows:

a-Methylglutaconic Acid, $CO_2H{\cdot}CHMe{\cdot}CH{:}CH{\cdot}CO_2H$.—This acid has been prepared by Conrad and Guthzeit (*Annalen*, 1883, **222**, 259), Ruhemann (Trans., 1893, **63**, 880), Smoluchowsky (*Monatsh.*, 1894, **15**, 56), and by Feist and Pomme (*Annalen*, 1909, **370**, 61). The stable form of the acid is undoubtedly the *trans*-*modification, which melts, as found by Feist and Pomme, at 145—146°. This is, moreover, the chief form in which the acid is obtained, both by the acid or alkaline hydrolysis of its esters. The last-named investigators were unable to cause the acid to react with acetyl chloride, but prepared an anhydride, melting at 85°, through the agency of phosphorus pentachloride. From this anhydride they prepared a semianilide, melting at 165°, and an unstable *cis*-acid, melting at 118°. They also prepared an anil, melting at 229°, by treating the acid of higher melting point with aniline at 150°.

a-Ethylglutaconic Acid, $CO_2H{\cdot}CHEt{\cdot}CH{:}CH{\cdot}CO_2H$.—This acid has been prepared by Guthzeit and Dressel (*Ber.*, 1890, **23**, 3188). The melting point is given as 118—120°, but, as we have shown in Part I. of this series, this is much too low, and the acid when pure melts at 133—134°. No other derivatives of this acid have been described.

a-Benzylglutaconic Acid, $CO_2H{\cdot}CH(CH_2Ph){\cdot}CH{:}CH{\cdot}CO_2H$.—This acid has been prepared by Conrad and Guthzeit (*Annalen*, 1883, **222**, 261), Ruhemann (Trans., 1893, **63**, 259), Guthzeit and Laska (*J. pr. Chem.*, 1896, [ii], **54**, 369), and by Guthzeit and Bolam (*ibid.*, 1898, [ii], **58**, 428). We find the melting point to be 153—154°, which is a little higher than that previously recorded. No derivatives of this acid seem to have been described.

We have selected these three acids for experiment as being typical of the *a*-monosubstituted derivatives of glutaconic acid, and the results of our experiments are briefly as follows:

These compounds react with acetyl chloride at the temperature of the boiling reagent, but under these conditions the interaction is slow, and is rarely complete. In sealed tubes at 100°, however, the action is rapid, and after four hours no unchanged acid remains. The product is not the true anhydride, but is a mixture

* The terms *cis*- and *trans*- are used in this paper in connexion with the acids of classes II and III for the sake of convenience pending a discussion of the subject in a subsequent part of the series. For the same reason the older formulae for the "mobile" acids are retained in the introduction to this part.

f two substances, one of which is the hydroxy-anhydride (I), the ther the chloro-anhydride (II):

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CR{-}{-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big\rangle\mathrm{O} \qquad\qquad \mathrm{CH}\Big\langle\begin{matrix}\mathrm{CR{-}CO}\\ \mathrm{CH{:}CCl}\end{matrix}\Big\rangle\mathrm{O}$$

(I.) (II.)

These compounds are, of course, derivatives of α-pyrone, and are so named in the experimental portion of this section, but their close relationship to the substituted glutaconic acid renders it advisable to adopt the names hydroxy-anhydride and chloro-anhydride when referring to them in the introduction.

The proportion in which these substances are formed depends entirely on the time during which the reagent is allowed to react, and on prolonged heating at 100° the chloro-anhydride is the sole product. The mechanism of this abnormal reaction is probably thus: The first action of acetyl chloride produces the normal anhydride, but at the temperature of the reaction the mobile hydrogen atom passes outside the three-carbon system to the neighbouring carbonyl group, where it is slowly attacked by acetyl chloride, yielding the acetyl-anhydride (III). This compound is, however, rapidly converted by the hydrogen chloride formed in the reaction into the chloro-anhydride, thus:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CR{-}CO}\\ \mathrm{CH_2{\cdot}CO}\end{matrix}\Big\rangle\mathrm{O} \longrightarrow \mathrm{CH}\Big\langle\begin{matrix}\mathrm{CR{-}{-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}\Big\rangle\mathrm{O} \longrightarrow$$

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{CR{-}{-}CO}\\ \mathrm{CH{:}C(OAc)}\end{matrix}\Big\rangle\mathrm{O} \longrightarrow \mathrm{CH}\Big\langle\begin{matrix}\mathrm{CR{-}CO}\\ \mathrm{CH{:}CCl}\end{matrix}\Big\rangle\mathrm{O}$$

(III.)

Strong support is given to this view, because in one case (that of αβ-dimethylglutaconic acid) we were able to isolate the acetyl-anhydride, and to show that it was an intermediate product in the transformation of the hydroxy-anhydride into the chloro-anhydride.

As the behaviour of the derivatives of the three acids is much the same, and is only modified by the presence of the heavier grouping, the general properties of these curious substances can be indicated by referring to the α-benzyl derivatives.

The mixture of the hydroxy-anhydride and chloro-anhydride obtained by heating α-benzylglutaconic acid with acetyl chloride, is readily separated by means of ether:

$$\mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph){\cdot}CO}\\ \mathrm{CH{=}{=}C(OH)}\end{matrix}\Big\rangle\mathrm{O} \qquad\qquad \mathrm{CH}\Big\langle\begin{matrix}\mathrm{C(CH_2Ph){\cdot}CO}\\ \mathrm{CH{=}{=}{=}CCl}\end{matrix}\Big\rangle\mathrm{O}$$

M. p. 90°. M. p. 74°.

The hydroxy-anhydride acts as a monobasic acid, and is characterised by giving a crystalline monopotassium salt (IV), which is very soluble in water, and the solution when acidified again yields

the hydroxy-anhydride. These changes can therefore be represented thus:

$$\mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}\right>\mathrm{O}\ \underset{\text{acid}}{\overset{\text{alkali}}{\rightleftarrows}}\ \mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OK)}\end{matrix}\right>\mathrm{O}$$

(IV.)

When the chloro-anhydride is treated with excess of aqueous potassium hydroxide it is ultimately converted into the sparingly soluble potassium salt of the hydroxy-pyrone, from which the hydroxy-anhydride is obtained on acidifying:

$$\mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=\!=}CCl}\end{matrix}\right>\mathrm{O}\ \xrightarrow{\text{KOH}}\ \mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OK)}\end{matrix}\right>\mathrm{O}\ \rightarrow$$
$$\mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{C{=\!=\!=}C(OH)}\end{matrix}\right>\mathrm{O}$$

When the hydroxy-anhydride is warmed with excess of potassium hydroxide, it is slowly converted into the dipotassium salt of the *cis*-acid. This acid melts at 139°, and is completely transformed into the *trans*-modification of the acid * when it is boiled for a few minutes with hydrochloric acid:

$$\mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}\right>\mathrm{O}\ \rightarrow\ \begin{matrix}\mathrm{CH_2Ph\cdot C\cdot CO_2H}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}\ \rightarrow\ \begin{matrix}\mathrm{CO_2H\cdot C\cdot CH_2Ph}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

M. p. 139°. M. p. 153—154°.

When the hydroxy-anhydride is boiled with alcohol it is converted into the acid ester:

$$\mathrm{CH}\left<\begin{matrix}\mathrm{C(CH_2Ph)\cdot CO}\\ \mathrm{CH{=\!=}C(OH)}\end{matrix}\right>\mathrm{O}\ +\ \mathrm{ROH}\ \rightarrow\ \begin{matrix}\mathrm{CH_2Ph\cdot C\cdot CO_2Et}\\ \|\\ \mathrm{CH}\\ |\\ \mathrm{CH_2\cdot CO_2H}\end{matrix}$$

The hydroxy-anhydrides and the chloro-anhydrides from the α-methyl and α-ethyl acids behave in an analogous manner, but the stability of the anhydride increases with the weight of the group attached to the α-carbon atom; thus the hydroxy-anhydride from the α-methyl acid is rapidly converted into the salt of the *trans*-acid when it is dissolved in excess of sodium hydrogen carbonate solution at the ordinary temperature, and the titration of this substance has therefore to be effected very quickly, otherwise the figures obtained are too high. The hydroxy-anhydride from the α-ethyl acid is much more stable, and can be titrated without any special precautions; but it is slowly converted into the salt of the *cis*-acid in the presence of excess of sodium hydrogen carbonate solution. The stability of the *cis*-forms of these acids increases with the molecular weight of the group occupying the α-position.

* See footnote, p. 2210.

but the *cis*-form is always produced when the anhydride is hydrolysed by strong alkali hydroxide or by alkali carbonates in the presence of casein.

In the above description of the hydroxy-anhydrides and chloro-anhydrides it will be noticed that we have assigned to them a constitution in which the substituting group is attached to the carbon atom. It is, of course, obvious that in these substances the double bonds must be fixed, and that the virtual tautomerism of the glutaconic acid ceases when the mobile hydrogen passes outside the three-carbon system. There must, therefore, be two forms of these compounds, which can be represented in the case of the hydroxy-anhydride by the formulæ V and VI:

$$\underset{\text{(V.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{CR{-\!\!-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O}} \qquad \text{and} \qquad \underset{\text{(VI.)}}{\mathrm{CH}{<}\begin{matrix}\mathrm{CR{:}C(OH)}\\ \mathrm{CH{-\!\!-\!\!-}CO}\end{matrix}{>}\mathrm{O}}$$

We are satisfied that the compounds described by us have a structure represented by formula V, because they yield no trace of a pyruvic acid on oxidation, but give oxalic acid as chief product. It is probable that compounds constituted as in formula VI would give pyruvic acid or a homologue under these conditions.

The normal anhydrides of the α-substituted glutaconic acids are formed, as Feist and Pomme (*loc. cit.*) have shown in the case of the α-methyl acid, by treating the acid with sufficient phosphorus pentachloride to convert it into the monoacid chloride when a reaction ensues, which is represented by the equation:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CHR{\cdot}CO_2H}\\ \mathrm{CH{\cdot}COCl}\end{matrix} \quad \rightarrow \quad \mathrm{CH}{<}\begin{matrix}\mathrm{CHR{\cdot}CO}\\ \mathrm{CH{-}CO}\end{matrix}{>}\mathrm{O} + \mathrm{HCl}.$$

Under these conditions, therefore, the mobile hydrogen atom remains within the three-carbon system, but we find that these normal anhydrides are without exception converted into the hydroxy-anhydrides on distillation, thus:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CHR{\cdot}CO}\\ \mathrm{CH{-}CO}\end{matrix}{>}\mathrm{O} \quad \longrightarrow \quad \mathrm{CH}{<}\begin{matrix}\mathrm{CR{-\!\!-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O}.$$

The Aniline Derivatives of the α-Substituted Glutaconic Acids.—Up to the present time the only derivatives of this type which have been described are a semianilide, melting at 165°, which Feist and Pomme prepared from the normal anhydride of α-methylglutaconic acid, and an anil melting at 229°, which the same chemists prepared by heating α-methylglutaconic acid with one molecule of aniline at 150°. We have tried on several occasions to prepare the anil melting at 229°, but we have always obtained a semianilide melting at 189°. We therefore sent a small quantity of α-methylglutaconic acid to Professor Feist and asked him to prepare for us some of his anil. Strangely enough, he also obtained our semianilide melting

at 189°, and it is evident, therefore, that the preparation of the anil depends on conditions which cannot be easily reproduced. During our many experiments with α-methylglutaconic acid we have not as yet succeeded in isolating any aniline derivative having this melting point, and the structure of this substance must therefore remain for the present unsolved. The *trans*-modifications of α-methyl-, α-ethyl-, and α-benzyl-glutaconic acids behave in a precisely similar manner when heated with aniline at 150°, and yield well-defined semianilides, which, since they lose carbon dioxide when heated a few degrees above their melting points, yielding anilides of monobasic acids, are probably constituted in accordance with formula VIII:

$$\begin{array}{l} CO_2H\cdot CH\cdot R \\ \quad \vert \\ \quad CH \\ \quad \Vert \\ \quad CH\cdot CO\cdot NHPh \\ \quad (VII). \end{array} \qquad\qquad \begin{array}{l} CO_2H\cdot CH_2 \\ \quad \vert \\ \quad CH \\ \quad \Vert \\ R\cdot C\cdot CO\cdot NHPh \\ \quad (VIII.) \end{array}$$

The only other formula for a semianilide losing carbon dioxide in this manner would be formula VII. That the semianilides prepared by us have a structure represented by formula VIII is proved by the formation of malonic acid from them on oxidation. It is clear that a compound of formula VII would give the alkylmalonic acid when oxidised.

The *cis*-modifications of the three α-substituted acids also give, on heating with aniline,* the *trans*-modifications of the semianilides identical with those prepared from the *trans*-acids, and it is evident, therefore, that a complete rearrangement to the stable *trans*-form occurs at the temperature of the reaction. The *cis*-modification of the semianilide can, however, be readily prepared from the hydroxy-anhydrides by warming them in benzene solution with aniline, thus:

$$CH{<}\begin{array}{l} CR\text{——}CO \\ CH{:}C(OH) \end{array}{>}O \longrightarrow \begin{array}{l} R\cdot C\cdot CO\cdot NHPh \\ \quad \Vert \\ \quad CH \\ \quad \vert \\ \quad CH{:}C(OH)_2 \end{array} \longrightarrow \begin{array}{l} R\cdot C\cdot CO\cdot NHPh \\ \quad \Vert \\ \quad CH \\ \quad \vert \\ \quad CH_2\cdot CO_2H \end{array}$$

The structure of these substances is clear from the fact that on heating at 150° they are completely transformed into the *trans*-semianilides; thus the α-methyl derivative behaves as follows:

$$\begin{array}{l} Me\cdot C\cdot CO\cdot NHPh \\ \quad \Vert \\ \quad CH \\ \quad \vert \\ \quad CH_2\cdot CO_2H \\ \quad \text{M. p. 148°.} \end{array} \xrightarrow{150°} \begin{array}{l} NHPh\cdot CO\cdot C\cdot Me \\ \qquad\qquad \Vert \\ \qquad\qquad CH \\ \qquad\qquad \vert \\ \qquad\qquad CH_2\cdot CO_2H \\ \qquad\qquad \text{M. p. 189°.} \end{array}$$

* It is probable, and it is assumed, that these anilic acids represent true maleic and fumaric forms, and that in them the double bond is fixed.

The *cis*-semianilides prepared from the hydroxy-anhydrides are not the same compounds as are obtained from the normal anhydride and aniline; thus the *trans*-semianilide from α-methylglutaconic acid melts at 189°, whilst the *cis*-semianilide from the hydroxy-anhydride melts at 148°. The semianilide formed from the normal anhydride by Feist and Pomme melts at 165°. It is probable that this substance is formed in accordance with the following equation (see p. 2220):

$$CH{\lessdot}^{CHMe\cdot CO}_{CH—CO}{>}O \longrightarrow \begin{array}{l} Me\cdot CH\cdot CO\cdot NHPh \\ \quad CH \\ \quad CH\cdot CO_2H \end{array}$$

M. p. 165°.

The normal anhydrides of these acids are, however, so difficult to prepare that we have not as yet been able to obtain enough of this semianilide to enable us to study the products formed from it on oxidation.

The derivatives of the α-monosubstituted glutaconic acids may therefore be summarised as follows:

	trans-Form.	*cis*-Form.	Normal anhydride.	Hydroxy-anhydride.	Chloro-anhydride.	*cis*-Semianilide.	*trans*-Semianilide	Semianilide from normal anhydride.
α-Methylglutaconic acid, $CO_2H\cdot CMe\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H$ ...	145—146°	118°	85°	74·5°	71°	148°	189°	165°
α-Ethylglutaconic acid, $CO_2H\cdot CEt\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H$ ...	133—134	108	liquid	liquid B.p. 175°/23.	39	121	170	149
α-Benzylglutaconic acid, $CO_2H\cdot C(CH_2Ph)\cdot CH(\mathbf{H})\cdot CH\cdot CO_2H$	153—154	139	—	90·0	74	143	175	—

The conclusion to be drawn from these experiments is that the stable form of the α-substituted acid and its derivatives at low temperatures contains the mobile hydrogen atom in the three-carbon system, but that at high temperatures the hydrogen atom passes to the carbonyl oxygen.

(*b*) *The Disubstituted Derivatives.*—There are four acids of this type known:

αβ-Dimethylglutaconic acid, $CO_2H\cdot CMe\cdot CMe(\mathbf{H})\cdot CH\cdot CO_2H$, has been prepared by Rogerson and Thorpe (Trans., 1905, **87**, 1696) and by Feist and Beyer (*Annalen*, 1906, **345**, 117). The acid melts at 148°, and gives a liquid anhydride boiling at 163°/15 mm.*; the semianilide prepared from this anhydride melts at 139°.

αγ-Dimethylglutaconic acid, $CO_2H\cdot CMe\cdot CH(\mathbf{H})\cdot CMe\cdot CO_2H$, was

* Through a clerical error the pressure given in the original paper was 25 mm.

first prepared by Reformatzky (*J. Russ. Phys. Chem. Soc.*, 1898, **30**, 453), and subsequently by Blaise (*Bull. Soc. chim.*, 1903, [iii], **29**, 1016; *Compt. rend.*, 1903, **136**, 381, 692, 1140). It has been more recently investigated by Feist and Reuter (*Annalen*, 1909, **370**, 82), but these chemists were unable to cause the acid to react with acetyl chloride.

β-Methyl-α-ethylglutaconic acid, $CO_2H{\cdot}CEt{\cdot}CMe(H){\cdot}CH{\cdot}CO_2H$ has been prepared by Rogerson and Thorpe (Trans., 1905, **87**, 1709). It melts at 164°, gives an anhydride melting at 53°, and a semianilide melting at 129°.

α-Methyl-γ-ethylglutaconic acid, $CO_2H{\cdot}CMe{\cdot}CH(H){\cdot}CEt{\cdot}CO_2H$ is described in Part I. of this series (this vol., p. 2197).

Of these acids we propose here to describe only the *αβ*- and *αγ*-dimethyl derivatives, leaving the other acids of this series to be dealt with in a subsequent paper.

It is certainly remarkable that Feist and Reuter should have been unable to cause the *αγ*-dimethyl acid to react with acetyl chloride, because in our hands interaction between these substances proceeded smoothly and rapidly at the temperature of the boiling reagent. The probable cause of this discrepancy has revealed itself during some recent experiments with glutaconic acid. This acid does not react with Kahlbaum's pure acetyl chloride under the conditions given by Buchner (*Ber.*, 1894, **27**, 382), but readily does so with Kahlbaum's "Acetyl chloride II." The presence of traces of phosphorus trichloride or phosphoryl chloride in the less pure reagent presumably acts as a "catalyst."

αβ-Dimethylglutaconic Acid.—This acid is converted into the anhydride when it is heated a few degrees above its melting point. The anhydride is also formed when the acid is heated for from ten to fifteen minutes on the water-bath with acetyl chloride, but under these conditions the product consists for the most part of the hydroxy-anhydride, and is composed entirely of this substance if the heating with acetyl chloride is continued for one hour. As, moreover, the normal anhydride is completely converted into the hydroxy-anhydride on distillation, it is evident that the compound described in the former paper as the normal anhydride must be the hydroxy-anhydride of formula IX. This conclusion was tested by a titration of the anhydride, when figures corresponding with the formation of the salt of the hydroxy-pyrone (X) were obtained:

$$CMe{<}{\begin{matrix}CMe{-\!\!-}CO\\ CH{:}C(OH)\end{matrix}}{>}O \quad \underset{\text{alkali}}{\overset{\text{acids}}{\rightleftarrows}} \quad CMe{<}{\begin{matrix}CMe{-\!\!-}CO\\ CH{:}C(ONa)\end{matrix}}{>}O$$

(IX.) (X.)

When the cold neutral solution of the salt is acidified, the hydroxy-anhydride is again precipitated, and at the ordinary

temperature there appears to be little tendency for the mobile hydrogen atom to re-enter the three-carbon system; but this change takes place with great rapidity when the solution is boiled, yielding the sodium hydrogen salt of the original acid *:

$$\mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{-\!-}CO}\\\mathrm{CH{:}C(ONa)}\end{matrix}}{>}\mathrm{O} + \mathrm{H_2O} \longrightarrow \mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{\cdot}CO_2H}\\\mathrm{CH_2{\cdot}CO_2Na}\end{matrix}} \longrightarrow$$

$$\mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{\cdot}CO_2H}\\\mathrm{CH_2{\cdot}CO_2H}\end{matrix}}$$

M.p. 148°.

If, therefore, the $\alpha\beta$-dimethyl acid is heated for one hour with acetyl chloride, the product after removing the reagent can be extracted entirely from its solution in ether by aqueous sodium hydrogen carbonate. After heating for six hours a considerable quantity of solid remains dissolved in the ether, and this was proved to be the acetyl-anhydride (XI). No trace of the chloro-anhydride is formed under these conditions:

$$\mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{-\!-}CO}\\\mathrm{CH{:}C(OH)}\end{matrix}}{>}\mathrm{O} \longrightarrow \mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{-\!-}CO}\\\mathrm{CH{:}C(OAc)}\end{matrix}}{>}\mathrm{O} \longrightarrow$$

M.p. 65°.
(XI.)

$$\mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{\cdot}CO}\\\mathrm{CH{:}CCl}\end{matrix}}{>}\mathrm{O}.$$

The acetyl-anhydride is readily hydrolysed to the acid from which it was derived, and its formation clearly indicates the mechanism of the reactions by which the chloro-anhydrides are produced. The chloro-anhydride of the $\alpha\beta$-dimethyl acid is difficult to prepare, but is obtained in small amount by the prolonged action of acetyl chloride at 100°, and is, moreover, formed when the acetyl anhydride is heated in a sealed tube with a solution of hydrogen chloride in acetic acid. Apart from other considerations the constitution of the acetyl-anhydride is shown by the formation of acetanilide and the semianilide of $\alpha\beta$-dimethylglutaconic acid when it is treated with excess of aniline:

$$\mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{-\!-}CO}\\\mathrm{CH{:}C(OAc)}\end{matrix}}{>}\mathrm{O} + 2\mathrm{NH_2Ph} \longrightarrow$$

$$\mathrm{CMe}{<}{\begin{matrix}\mathrm{CMe{\cdot}CO_2H}\\\mathrm{CH_2{\cdot}CO{\cdot}NHPh}\end{matrix}} + \mathrm{NHAcPh}.$$

$\alpha\gamma$-*Dimethylglutaconic Acid.*—This acid readily yields the normal anhydride, and it is therefore evident that the presence of a second methyl group attached to the γ-carbon atom has a marked restraining effect on the tendency of the mobile hydrogen atom to remain outside the three-carbon system. The normal

* Incidentally these reactions are clearly another proof of the identity of the α- and γ-positions.

anhydride can be quantitatively converted into the crystalline hydroxy-anhydride by heating:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CHMe{\cdot}CO}\\ \mathrm{CMe{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}\!{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CMe{:}CCl}\\ \mathrm{CMe{-}CO}\end{matrix}{>}\mathrm{O}$$

M.p. 74°. M.p. 82–83°.

The hydroxy-anhydride is readily produced when the acid is heated with acetyl chloride at 100°, and at the same time there is formed a small quantity of the chloro-anhydride, melting at 82—83°, which is undoubtedly the same substance as that prepared in small quantity by Feist and Reuter (*Annalen*, 1909, **370**, 84) by the action of phosphorus pentachloride on the acid. The formation of the acetyl-anhydride could not be detected, and it is evident that the acetylation, and therefore chlorination, of the hydroxy-anhydride takes place with great difficulty.

The hydroxy-anhydride on titration gives figures closely approximating to those required for the monobasic hydroxy-pyrone, but even at the ordinary temperature the passage of the mobile hydrogen atom into the three-carbon system is very rapid, and the change is complete in the course of a few minutes:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CMe{:}C(OH)}\\ \mathrm{CMe{-}\!{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \mathrm{CH}{<}\begin{matrix}\mathrm{CMe{:}C(OK)}\\ \mathrm{CMe{-}\!{-}CO}\end{matrix}{>}\mathrm{O} \longrightarrow \begin{matrix}\mathrm{Me{\cdot}CH{\cdot}CO_2H}\\ \mathrm{CH}\\ \mathrm{Me{\cdot}C{\cdot}CO_2H}\end{matrix}$$

The acid produced is again the only known form of the acid.

The Aniline Derivatives of the Members of Section (b).—The fact that the stable form of the acids of this class form anhydrides with greater ease than the mono-α-substituted derivatives, enables them to form certain interesting derivatives with aniline, a study of which throws considerable light on the properties conferred on these compounds by the presence of the mobile hydrogen atom; for example, the hydroxy-anhydride of αβ-dimethylglutaconic acid yields a semianilide melting at 139°:

$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}\!{-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O} \longrightarrow \begin{matrix}\mathrm{Me{\cdot}C{\cdot}CO_2H}\\ \mathrm{Me{\cdot}\overset{\|}{C}}\\ \mathrm{\overset{|}{C}H_2{\cdot}CO{\cdot}NHPh}\end{matrix}$$

M. p. 139°.

which gives an hydroxy-anil in accordance with the scheme:

$$\begin{matrix}\mathrm{Me{\cdot}C{\cdot}CO_2H}\\ \mathrm{Me{\cdot}\overset{\|}{C}}\\ \mathrm{\overset{|}{C}H_2{\cdot}CO{\cdot}NHPh}\end{matrix} \longrightarrow \mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}\!{-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{NPh}$$

Semianilide, m. p. 139°. Hydroxy-anil, m. p. 125°.

The hydroxy-anil behaves in the same manner as the hydroxy-anhydrides, and titrates as a monobasic acid. The neutral solution regenerates the hydroxy-anil when acidified, and it is therefore evident that the change must be represented by the scheme:

$$\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}{-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{NPh} \quad \underset{\text{acids}}{\overset{\text{alkali}}{\rightleftarrows}} \quad \mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}{-}CO}\\ \mathrm{CH{:}C(OK)}\end{matrix}{>}\mathrm{NPh}.$$

We have not yet succeeded in finding the conditions under which this substance is converted into the semianilide or normal anil, that is to say, the conditions which cause the mobile hydrogen atom to pass into the three-carbon system, and it is therefore evident that with the $\alpha\beta$-disubstituted derivatives the tendency for the mobile hydrogen atom to remain outside the three-carbon system is very considerable. Further experiments on the $\alpha\beta$-dimethyl acid and on higher members of the series are in progress, but so far we have not been able to prepare the normal anhydride of any of these acids in a pure condition.

With the $\alpha\gamma$-disubstituted derivatives the attachment of an alkyl group to the γ-carbon atom so far modifies the mobility of the hydrogen atom as to cause both forms to be stable. This decreased mobility, which is indicated by the ready manner in which both the normal and hydroxy-anhydrides can be isolated from $\alpha\gamma$-dimethylglutaconic acid, causes this acid, in the form of its aniline derivatives, to exhibit properties which may be regarded as typical of a compound belonging to this class, in which a state of equilibrium within the molecule enables either the one form or the other to be capable of isolation, and to be readily convertible the one into the other; thus, when the normal anhydride of $\alpha\gamma$-dimethylglutaconic acid is treated with aniline, a semianilide is formed, which when heated at 150° passes with loss of water into the hydroxy-anil:

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CMe{-}{-}CO}\\ \mathrm{CHMe{\cdot}CO}\end{matrix}{>}\mathrm{O} \quad \longrightarrow \quad \mathrm{CH}{<}\begin{matrix}\mathrm{CMe{\cdot}CO_2H}\\ \mathrm{CHMe{\cdot}CO{\cdot}NHPh}\end{matrix}$$

M. p. 165—166°.

$$\mathrm{CH}{<}\begin{matrix}\mathrm{CMe{-}{-}CO}\\ \mathrm{CMe{:}C(OH)}\end{matrix}{>}\mathrm{NPh}$$

M. p. 112°.

This hydroxy-anil behaves as a monobasic acid, and if the cold neutral solution of the salt is acidified, the unaltered anil is precipitated. If, however, the neutral solution is raised to the boiling point and then acidified, the semianilide (m. p. 166°) is obtained as sole product, showing that at 100° the re-entry of the mobile hydrogen atom into the three-carbon system with fission of

the ring is complete. This change may therefore be represented as follows:

$$\mathrm{CH}{<}\substack{\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CMe{:}C(OH)}}{>}\mathrm{NPh} \underset{\mathrm{acids}}{\overset{\mathrm{alkali}}{\rightleftarrows}} \mathrm{CH}{<}\substack{\mathrm{CMe{\cdot}CO_2K}\\ \mathrm{CMe{:}C(OH){\cdot}NHPh}}$$

$$\xrightarrow{100^\circ} \mathrm{CH}{<}\substack{\mathrm{CMe{\cdot}CO_2K(H)}\\ \mathrm{CHMe{\cdot}CO{\cdot}NHPh}}$$

The increased stability of the "normal" forms of these compounds causes them, moreover, to exhibit a further interesting change; thus, when a solution of the hydroxy-anil in excess of alkali is titrated with hydrochloric acid, using phenolphthalein as indicator, a definite end-point is reached corresponding with the formation of the alkali salt of the hydroxy-pyrone. On remaining for a few moments the colour of the indicator returns, showing that the solution has become again alkaline. More acid may then be added, when the colour again returns on keeping, and this process may be repeated until finally the solution remains neutral. At this stage a considerable quantity of crystalline material separates; this substance is the true anil of the acid. The filtrate from the crystalline anil yields the hydroxy-anil when acidified, and from this recovered substance more of the anil may be prepared by repeating the above process.

It is probable that this behaviour is due to the dissociation of the alkali salt in neutral solution, and the consequent migration of the mobile hydrogen atom, thus:

$$\mathrm{CH}{<}\substack{\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CMe{:}C(OK)}}{>}\mathrm{NPh} \rightarrow \mathrm{CH}{<}\substack{\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CMe{:}C(OH)}}{>}\mathrm{NPh} \rightarrow$$

$$\mathrm{CH}{<}\substack{\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CHMe{\cdot}CO}}{>}\mathrm{NPh}$$

There is one point respecting the semianilides of the substituted glutaconic acid which requires a brief explanation. It will be remembered that the semianilide prepared by Feist and Pomme from the normal anhydride of α-methylglutaconic acid melts at 165°, and is not the same compound as that prepared by us from the hydroxy-anhydride and aniline, which melts at 148°, and is converted on heating into the *trans*-semianilide, melting at 189°.

On the other hand, the semianilides prepared from the normal anhydride and the hydroxy-anhydride of αγ-dimethylglutaconic acid and aniline are, as already mentioned, identical. The explanation of this apparent discrepancy is, however, obvious, because it is evident that, whereas there are two possible forms of the hydroxy-anhydride of α-methylglutaconic acid, namely:

$$\mathrm{CH}{<}\substack{\mathrm{CMe{:}C(OH)}\\ \mathrm{CH{-\!\!-}CO}}{>}\mathrm{O} \quad \text{and} \quad \mathrm{CH}{<}\substack{\mathrm{CH{:}C(OH)}\\ \mathrm{CMe{-\!\!-}CO}}{>}\mathrm{O}$$

there is only one possible modification of the hydroxy-anhydride of αγ-dimethylglutaconic acid, as also of the hydroxy-anil:

$$CH{<}\begin{matrix}CMe{:}C(OH)\\ CMe{-\!-}CO\end{matrix}{>}O \quad \text{and} \quad CH{<}\begin{matrix}CMe{:}C(OH)\\ CMe{-\!-}CO\end{matrix}{>}NPh.$$

The semianilide which is formed from this hydroxy-anil must therefore have the structure:

$$\underset{\text{Hydroxy-anil.}}{CH{<}\begin{matrix}CMe{:}C(OH)\\ CMe{-\!-}CO\end{matrix}{>}NPh} \longrightarrow \underset{\text{Semianilide.}}{CH{<}\begin{matrix}CHMe{\cdot}CO{\cdot}NHPh\\ CMe{\cdot}CO_2H\end{matrix}}$$

This, it will be noticed, is the same formula as that which we have assigned to the semianilide prepared by Feist and Pomme (see p. 2215), and it is evident, therefore, that the normal anhydrides behave in the same manner in both cases.

The derivatives of the acids of section (*b*) may be therefore summarised as follows:

	Acid.	Normal anhydride.	Hydroxy anhydride.	Chloro-anhydride.	Hydroxy-anil.	Semianilide.	Anil.
αβ-Dimethylglutaconic acid $CO_2H{\cdot}CMe{:}CMe(H){\cdot}CH{\cdot}CO_2H$	148°	—	B. p. 188°/25 mm.	liquid B.p. 133°/26 mm.	125°	139°	—
αγ-Dimethylglutaconic acid $CO_2H{\cdot}CMe{:}CH(H){\cdot}CMe{\cdot}CO_2H$	147	liquid	75	82–83	112	166	174

The Acids of Section (*c*).—The only acid of this kind which is at present known is αβγ-trimethylglutaconic acid,

$$CO_2H{\cdot}CMe{\cdot}CMe(H){\cdot}CMe{\cdot}CO_2H,$$

which was prepared by Rogerson and Thorpe (Trans., 1905, **87**, 1704). The acid melts at 127°, and gives an anhydride when boiled with acetic anhydride, which melts at 119°. As in the case of the αβ-dimethyl acid, there is no doubt that this anhydride is the hydroxy-anhydride. The normal anhydride is a liquid, and is formed by the action of boiling acetyl chloride on the acid. The normal anhydride is quite insoluble in aqueous sodium hydrogen carbonate, and when distilled is completely converted into the hydroxy-anhydride:

$$CMe{<}\begin{matrix}CHMe{\cdot}CO_2H\\ CMe{\cdot}CO_2H\end{matrix} \xrightarrow{\text{acetyl chloride}} \underset{\text{Liquid.}}{CMe{<}\begin{matrix}CHMe{\cdot}CO\\ CMe{-}CO\end{matrix}{>}O} \xrightarrow{\text{distillation}}$$

$$\underset{\text{M. p. 119°.}}{CMe{<}\begin{matrix}CMe{:}C(OH)\\ CMe{-\!-}CO\end{matrix}{>}O}$$

No trace of the chloro-anhydride or acetyl-anhydride could be detected among the products formed in these reactions. The hydroxy-anhydride exhibits all the properties of the other members of the series; thus, when rapidly titrated it yields figures corresponding with those required for the hydroxy-pyrone, but the

neutral solution of the salt rapidly changes on keeping, yielding the monoalkali salt of the original acid:

$$\mathrm{CMe}\begin{cases}\mathrm{CMe{:}C(OH)} \\ \mathrm{CMe{-\!-\!-}CO}\end{cases}\!\!>\mathrm{O} \longrightarrow \mathrm{CMe}\begin{cases}\mathrm{CMe{:}C(OK)} \\ \mathrm{CMe{-\!-\!-}CO}\end{cases}\!\!>\mathrm{O} \longrightarrow \mathrm{CMe}\begin{cases}\mathrm{CHMe{\cdot}CO_2K} \\ \mathrm{CMe{\cdot}CO_2K}\end{cases}$$

The Aniline Derivatives.—The behaviour of the $\alpha\beta\gamma$-trimethyl acid towards aniline is comparable with that of the $\alpha\gamma$-dimethyl acid, although it is evident that the presence of the methyl group on the β-carbon atom slightly increases the tendency for the mobile hydrogen atom to remain outside the three-carbon system; thus, when either the normal or hydroxy-anhydride is treated with aniline, the same semianilide is formed, and this compound when heated at 150° passes into the hydroxy-anil. The latter is also formed when the acid is heated with one molecular proportion of aniline at 150°. The tendency for the mobile hydrogen atom to pass back into the three-carbon system is, however, clearly shown by the fact that an alkaline solution of the hydroxy-anil slowly passes into the true anil and the semianilide, even at the ordinary temperature, and that the change is quickly completed if the solution is gently warmed. These reactions may therefore be represented in the following way:

$$\left.\begin{array}{l}\mathrm{CMe}\begin{cases}\mathrm{CMe{:}C(OH)} \\ \mathrm{CMe{-\!-\!-}CO}\end{cases}\!\!>\mathrm{O} \\ \mathrm{CMe}\begin{cases}\mathrm{CHMe{\cdot}CO} \\ \mathrm{CMe{-}CO}\end{cases}\!\!>\mathrm{O}\end{array}\right\} \longrightarrow \mathrm{CMe}\begin{cases}\mathrm{CMe{\cdot}CO{\cdot}NHPh} \\ \mathrm{CMe{\cdot}CO_2H}\end{cases} \underset{\text{alkali}}{\overset{\text{heating}}{\rightleftarrows}}$$

$$\mathrm{CMe}\begin{cases}\mathrm{CMe{:}C(OH)} \\ \mathrm{CMe{-\!-\!-}CO}\end{cases}\!\!>\mathrm{NPh} \longrightarrow \mathrm{CMe}\begin{cases}\mathrm{CHMe{\cdot}CO} \\ \mathrm{CMe{-}CO}\end{cases}\!\!>\mathrm{NPh}$$

The derivatives of this acid which we have prepared are:

	Acid. (*cis*-form).	Normal anhydride.	Hydroxy-anhydride.	Hydroxy-anil.	Semi-anilide.	[illegible]
$\alpha\beta\gamma$-Trimethylglutaconic Acid $\mathrm{CO_2H{\cdot}CMe{\cdot}CMe(H){\cdot}CMe{\cdot}CO_2H}$	127°	liquid	119°	103°	151°	[illegible]

It is desirable to emphasise the following conclusions which may be drawn from the above experiments:

(1) The tendency for the mobile hydrogen atom to pass to a neighbouring carbonyl group is clearly shown by the α-monosubstituted derivatives of glutaconic acid as soon as ring-formation is effected (and the necessary carbonyl group supplied) by transforming the acids into their anhydrides.

(2) The increase in weight of the group occupying the α-position increases the tendency for the mobile hydrogen atom to remain outside the three-carbon system.

(3) This phenomenon cannot be illustrated by the aniline deriv-

ative of the α-monosubstituted acids, because the *cis*-semianilides are converted into stable *trans*-modifications at a lower temperature than that required to throw the mobile hydrogen atom out of the three-carbon system.

(4) The presence of a methyl group at the β-carbon atom considerably increases the tendency for the mobile hydrogen atom to remain outside the three-carbon system.

(5) The presence of methyl groups at both the α- and γ-carbon atoms increases the tendency for the hydrogen atom to remain within the three-carbon system.

(6) The conditions which tend to throw the mobile hydrogen atom outside the three-carbon system are also the conditions which confer stability on the *cis*-form of the acids.

(7) The less stable *cis*-forms can be prepared from the hydroxy-anhydrides in the presence of excess of strong alkali, as well as by the aid of an "anticatalyst" (casein).

EXPERIMENTAL.

The cis-*Forms of the α-Monosubstituted Glutaconic Acids with their Normal Anhydrides, Hydroxy-anhydrides, and Chloro-anhydrides.*

cis-*α-Methylglutaconic Acid and its Normal Anhydride.*—These compounds have been fully described by Feist and Pomme (*Annalen*, 1909, **370**, 61).

The Hydroxy-anhydride of α-Methylglutaconic Acid (*6-Hydroxy-3-methyl-α-pyrone*), $CH<\begin{matrix}CMe—CO\\CH:C(OH)\end{matrix}>O$.

This compound may be prepared by the distillation of the normal anhydride under diminished pressure, but is more easily obtained by heating the acid with twice the theoretical quantity of acetyl chloride in a sealed tube at 100° for six hours. The product, after evaporating the excess of acetyl chloride on the water-bath, consists of about equal proportions of the hydroxy-anhydride and the chloro-anhydride, which can be separated by dissolving the mixture in dry ether and shaking the solution with aqueous sodium hydrogen carbonate until the lower layer is alkaline. The deep magenta-red aqueous solution is then quickly acidified, and the oil which separates is extracted by shaking once with ether. The hydroxy-anhydride is purified by distilling the ethereal residue under diminished pressure. It may also be obtained free from the chloro-anhydride by boiling the acid with excess of acetic anhydride for two hours and distilling the product, but in this case the formation of highly-coloured by-products considerably diminishes the yield.

The hydroxy-anhydride boils at 167°/18 mm. as a colourless oil, which solidifies on cooling. It crystallises from benzene in long prisms, melting at 74·5°:

0·1570 gave 0·3260 CO_2 and 0·0655 H_2O. C=56·78; H=4·65.
$C_6H_6O_3$ requires C=57·1; H=4·7 per cent.

The hydroxy-anhydride is sparingly soluble in cold water, but dissolves on warming, yielding a solution from which the anhydride partly separates on cooling. It is, however, slowly converted by warm water into the *trans*-form of the α-methyl acid. It dissolves in sodium hydrogen carbonate solution with effervescence, yielding the monoalkali salt of the hydroxy-pyrone, but at the same time a partial change into the dialkali salt of the normal acid ensues, a fact which is clearly shown by the following titration, in which the anhydride was dissolved in excess of standard alkali and titrated back by hydrochloric acid:

0·1902 required 36·6 c.c. of NaOH solution (1 c.c. = 0·0017 NaOH) for complete neutralisation. $C_6H_6O_3$ (monobasic) requires 35·34 c.c.*

The amount of alkali required for neutralisation increases with the time the alkaline solution of the salt is kept, and it is therefore evident that the change to the dialkali salt of the normal acid takes place fairly rapidly at the ordinary temperature. The neutral solution of the alkali salt of the hydroxy-pyrone formed in the above titration exhibits the characteristic property of all these substances of slowly developing a deep blue colour on keeping. This colour gradually changes through purple to red, and finally the solution becomes yellow. The silver salt of the monobasic acid, prepared through the ammonium salt, blackens almost at once.

The pure *cis*-form can be prepared by dissolving the anhydride in strong aqueous alkali, or by employing the "casein" method of Feist (compare *Annalen*, 1909, **370**, 52).

Oxidation.—The hydroxy-anhydride was oxidised in ice-cold alkaline solution by means of the requisite amount of permanganate. Oxalic acid was the only product which could be isolated.

The Chloro-anhydride of α-Methylglutaconic Acid (6-Chloro-3-methyl-α-pyrone), $CH\ll\begin{matrix}CMe\cdot CO\\CH{=}CCl\end{matrix}\gg O$.

The preparation of this compound has been partly described in the preceding section, since it remains in the ethereal solution after

* Better numbers can be obtained by dissolving the hydroxy-anhydride in cold alcohol and rapidly titrating with alkali direct; thus, 0·1712 required 31·9 c.c. of NaOH (1 c.c. = 0·0017 NaOH); $C_6H_6O_3$ requires 31·8 c.c. (monobasic).

all the acid constituents have been extracted by alkali. It is also produced in considerable quantities when the α-methyl acid is boiled with excess of acetyl chloride on the water-bath for four hours. In this case, however, some normal anhydride accompanies the halogen derivative, but owing to the ease with which the latter substance crystallises, it can be readily isolated in a pure condition by spreading on a porous plate. The chloro-anhydride distils without decomposition at 130°/25 mm., and the distillate sets to a solid mass on cooling. It shows a most marked tendency to crystallise, and can be obtained from light petroleum (b. p. 50—60°) in long, colourless prisms, melting at 71°:

0·2351 gave 0·4285 CO_2 and 0·0728 H_2O. C = 49·70; H = 3·45.
0·2344 „ 0·2330 AgCl. Cl = 24·58.

$C_6H_5O_2Cl$ requires C = 49·8; H = 3·5; Cl = 24·6 per cent.

The chloro-anhydride is readily soluble in benzene, and can be distilled under the ordinary pressure without decomposition. It is remarkably stable towards boiling water, and a small quantity separates unchanged when the hot aqueous solution is cooled. It is readily volatile with steam, but is slowly hydrolysed by boiling water and more quickly by aqueous alkalis.

Owing to the hydrogen chloride generated in the former process the acid produced is entirely the *trans*-modification, but in the presence of excess of strong alkali the *cis*-form is alone obtained. The action of excess of aniline on the chloro-anhydride in benzene solution yields a precipitate of aniline hydrochloride. The residue obtained on evaporating the filtered benzene solution gives a solid substance when rubbed with dilute hydrochloric acid, which crystallises from dilute alcohol in small, colourless needles, melting at 158°:

The compound is insoluble in aqueous alkaline carbonates, and would therefore appear to be the *anilide* of the acid,

NHPh·CO·CMe·CH(H)·CH·CO·NHPh:

0·1216 gave 0·3252 CO_2 and 0·0713 H_2O. C = 73·04; H = 6·54.

$C_{18}H_{18}O_2N_2$ requires C = 73·5; H = 6·1 per cent.

The action of aniline on the chloro-anhydride under other conditions will be described in a future communication.

cis-α-*Ethylglutaconic Acid*, $CO_2H·CEt·CH(H)·CH·CO_2H$.

Since this acid is much more stable than the corresponding *cis*-modification of α-methylglutaconic acid, it can be readily prepared either from the chloro-anhydride and aqueous potassium hydroxide or from the hydroxy-anhydride with the same reagent, but in this case also the presence of hydrochloric acid causes a

complete conversion of the *cis*- into the *trans*-modifications, and when therefore the chloro-anhydride is boiled with water or when it is left for a long time in contact with moist air, the *trans*-form of the acid melting at 133—134° is alone formed. The *cis*-acid is best prepared in quantity by dissolving the hydroxy-anhydride in excess of strong alkali, adding *N*-hydrochloric acid until neutral, and then warming the solution on the water-bath for a few minutes until a test portion gives no precipitate of unaltered hydroxy-anhydride on the addition of acid. The solution is then acidified when quite cold, and extracted by ether. The acid crystallises from chloroform in small prisms, melting at 108°:

0·2091 gave 0·4055 CO_2 and 0·1148 H_2O. C = 52·90; H = 6·12.

$C_7H_{10}O_4$ requires C = 53·2; H = 6·3 per cent.

The *silver* salt is a white, curdy precipitate:

0·2571 gave 0·1492 Ag. Ag = 58·03.

$C_7H_8O_4Ag_2$ requires Ag = 58·06 per cent.

The *cis*-acid is fairly stable towards hydrochloric acid unless the mineral acid is generated *in situ*, as is the case when the chloro-anhydride is treated with water. It can be recrystallised from equal proportions of concentrated hydrochloric acid and water, but if boiled for some time with this mixture gradual conversion of the *cis*- into the *trans*-form ensues, and the change is usually complete after heating for thirty minutes. The acid is very stable towards alkalis, and it may be boiled for a considerable time with excess of alkali hydroxide without undergoing change.

The Normal Anhydride of cis-α-*Ethylglutaconic Acid*,

$$CH(H){<}\begin{matrix}CEt\cdot CO\\ CH-CO\end{matrix}{>}O.$$

An attempt to prepare this substance by the action of acetyl chloride on the *cis*-acid yielded the hydroxy-anhydride as sole product. Ultimately the normal anhydride was prepared in small quantity by the action of phosphorus pentachloride on the *trans*-acid, the conditions employed being the same as those used by Feist and Pomme (*Annalen*, 1909, **370**, 69) for the preparation of the normal anhydride from *trans*-α-methylglutaconic acid. The anhydride is a liquid, insoluble in aqueous sodium hydrogen carbonate, and is completely converted into the hydroxy-anhydride on distillation under diminished pressure. It is therefore a matter of some difficulty to obtain this substance in a pure condition, but the following analysis was made of a specimen which had been purified by dissolving in ether and washing with sodium hydrogen carbonate solution:

0·1917 gave 0·4181 CO_2 and 0·1025 H_2O. C = 59·49; H = 5·94.

$C_7H_8O_3$ requires C = 60·0; H = 5·7 per cent.

The Hydroxy-anhydride of α-Ethylglutaconic Acid (6-*Hydroxy-3-ethyl-α-pyrone*), $CH{<}{\begin{matrix}CEt\text{---}CO\\CH{:}C(OH)\end{matrix}}{>}O$.

This compound is obtained, accompanied by the chloro-anhydride, by heating either the *cis*- or the *trans*-acid with twice the theoretical quantity of acetyl chloride in a sealed tube at 100° for six hours. The separation may be effected by evaporating the excess of chloride on the water-bath, dissolving the residue in pure ether, and shaking with aqueous sodium hydrogen carbonate until the lower layer is alkaline. The deep red alkaline solution deposits the anhydride as an oil when it is acidified, and this is then extracted by shaking once with ether. Some *cis*-acid, formed by the action of the alkali on the anhydride, is always extracted by this method, and it is therefore necessary to dissolve the ethereal residue in benzene, in which the *cis*-acid is quite insoluble, and filter in order to obtain the hydroxy-anhydride pure.

The anhydride distils as a mobile liquid at 176°/23 mm., and dissolves in aqueous sodium hydrogen carbonate with effervescence:

0·2513 gave 0·5052 CO_2 and 0·1146 H_2O. C = 59·52; H = 5·52.

$C_7H_8O_3$ requires C = 60·0; H = 5·7 per cent.

0·1540 required 36·8 c.c. of NaOH solution (1 c.c. = 0·001193 gram NaOH) for complete neutralisation. $C_7H_8O_3$ (monobasic) requires 36·9 c.c.

It is evident, therefore, that the tendency for the mobile hydrogen atom to pass back into the three-carbon system is less with this compound than with the corresponding methyl derivative; in fact, the hydroxy-anhydride is almost completely recovered when the cold neutral solution is acidified. If, however, the neutral solution is boiled, the change to the mono-alkali salt of the *cis*-acid is rapidly effected. The neutral solution slowly becomes deep blue with violet fluorescence when kept, the colour changing first to red and then to yellow on further keeping. The hydroxy-anhydride is completely converted into the *trans*-acid when boiled with dilute hydrochloric acid.

The Chloro-anhydride of α-Ethylglutaconic Acid (6-*Chloro-3-ethyl-α-pyrone*), $CH{<}{\begin{matrix}CEt{-}CO\\CH{:}CCl\end{matrix}}{>}O$.

The ethereal solution, after extracting the hydroxy-anhydride in the experiment described above, yields the chloro-anhydride on

evaporating. It can also be formed from the *trans*-acid by boiling it with excess of acetyl chloride for four hours, and is isolated in the same manner as in the sealed-tube experiment. By either process the anhydride is obtained as a liquid, which distils at 133°/23 mm. as a colourless oil, solidifying to a mass of crystals on cooling. The solid melts sharply at 39° after being in contact with porous porcelain, but as it is readily soluble in all "inert" solvents it cannot be recrystallised:

0·1890 gave 0·1700 AgCl. Cl = 22·25.

$C_7H_7O_2Cl$ requires Cl = 22·4 per cent.

The chloro-anhydride dissolves slowly in excess of strong alkali hydroxide, the solution becoming warm and red in colour. When all oil has passed into solution the immediate addition of acid causes the separation of an oil free from halogen, which proved on examination to be the pure hydroxy-anhydride.

If the alkaline solution is allowed to remain until no oil is precipitated by acid, ether extracts the *cis*-acid from the acidified solution.

cis-*α*-*Benzylglutaconic Acid*, $CO_2H\cdot C(CH_2Ph)\cdot CH(H)\cdot CH\cdot CO_2H$.

This acid is readily prepared, either by dissolving the chloro-anhydride in potassium hydroxide solution and acidifying, or by boiling the hydroxy-anhydride with strong alkali (see p. 2226). In this case also the presence of hydrogen chloride formed *in situ* causes a complete conversion of the *cis*- into the *trans*-modification, and thus when the chloro-anhydride is boiled with water the acid of higher melting point is alone formed. When prepared by either of the above methods, the *cis*-acid separates from water in slender needles, melting at 139°:

0·1826 gave 0·4350 CO_2 and 0·0884 H_2O. C = 65·30; H = 5·39.

$C_{12}H_{12}O_4$ requires C = 65·5; H = 5·5 per cent.

The acid is more soluble in warm water than the *trans*-modification.

The *silver* salt is a crystalline solid:

0·2941 gave 0·1462 Ag. Ag = 49·71.

$C_{12}H_{10}O_4Ag_2$ requires Ag = 49·77 per cent.

The *cis*-acid is completely converted into the *trans*-modification when boiled for half an hour with concentrated hydrochloric acid. In strong alkaline solution it may be boiled for several hours without undergoing change.

The normal anhydride of *α*-benzylglutaconic acid could not be prepared. The acid and phosphorus pentachloride react very slowly, and ultimately yields a product containing much chlorine, from which no definite substance could be isolated.

The Hydroxy-anhydride of α-Benzylglutaconic Acid (6-Hydroxy-3-benzyl-α-pyrone), $CH{<}{{C(CH_2Ph)\cdot CO}\atop{CH{=\!=}C(OH)}}{>}O$.

This substance is prepared by heating 5 grams of the *trans*-acid with 8 grams of acetyl chloride in a sealed tube at 100° for eight hours. The residue left on evaporating the excess of chloride yields the hydroxy-anhydride as a crystalline solid when rubbed with dry ether. It may be further purified by recrystallisation from a mixture of benzene and light petroleum (b. p. 50—60°), when it is obtained in long, flat needles, melting at 90°:

0·1444 gave 0·3748 CO_2 and 0·0634 H_2O. C = 71·02; H = 4·89.
$C_{12}H_{10}O_3$ requires C = 71·3; H = 5·0 per cent.

The *potassium* salt, $CH{<}{{C(CH_2Ph)\cdot CO}\atop{CH{=\!=}C(OK)}}{>}O$, is precipitated in glistening plates when a slight excess of aqueous potassium hydroxide is added to a solution of the hydroxy-anhydride in the same alkali. It crystallises from absolute alcohol in brilliant leaflets:

0·1876 gave 0·0675 K_2SO_4. K = 16·13.
$C_{12}H_9O_3K$ requires K = 16·25 per cent.

The alcoholic filtrate becomes deep blue on keeping.

The following titration of the hydroxy-anhydride was made, the anhydride being dissolved in excess of standard alkali and titrated back with standard acid:

0·2004 required 33·45 c.c. of NaOH solution (1 c.c. = 0·001193 gram NaOH) for neutralisation. $C_{12}H_{10}O_3$ (monobasic) requires 33·26 c.c.

The neutral solution becomes deep blue on keeping. That the cause of this colour is the oxygen of the air is shown by shaking a warm solution of the potassium salt with free access of air, when a deep purple solution is formed, from which a blue precipitate separates on keeping. The dried precipitate closely resembles indigo in appearance, but dissolves in alcohol, forming a fine blue solution.

The *silver* salt is precipitated as a white powder, which blackens immediately, even in red light. A satisfactory analysis could not be obtained.

The hydroxy-anhydride may also be prepared from the chloro-anhydride by warming it with excess of aqueous potassium hydroxide, when the formation of the insoluble potassium salt of the hydroxy-acid enables this change to be easily followed. The stability of the hydroxy-anhydride is very considerable, and it is necessary to heat it with excess of alkali for at least half an hour

before conversion into the alkali salt of the *cis*-acid is complete. The end-point of this change can be easily determined, because the presence of any unaltered "enol" form causes the separation of the insoluble potassium salt when the solution is cooled.

When the hydroxy-anhydride is boiled with alcohol, it is quickly transformed into the acid ester of the dibasic acid; thus with ethyl alcohol, *ethyl hydrogen α-benzylglutaconate*,

$$CO_2H\cdot C(CH_2Ph):CH\cdot CH_2\cdot CO_2Et,$$

is formed, which crystallises from dilute alcohol in slender needles, melting at 93°:

0·1096 gave 0·2714 CO_2 and 0·0636 H_2O. C = 67·53; H = 6·46.

$C_{14}H_{16}O_4$ requires C = 67·8; H = 6·4 per cent.

Since the acid ester is hydrolysed to the *cis*-acid by potassium hydroxide it probably retains the *cis*-configuration.

When the hydroxy-anhydride is boiled with dilute hydrochloric acid (one part of concentrated hydrochloric acid to one of water) it passes into solution, and a crystalline solid separates on cooling, which melts fairly sharply at 125°. Since this substance behaves on titration as a dibasic acid, it is probably an equilibrium mixture of the *cis*- and *trans*-modifications. Prolonged boiling with the mineral acid yields the *trans*-modification as sole product.

The Chloro-anhydride of α-Benzylglutaconic Acid (6-*Chloro-3-benzyl-α-pyrone*), $CH{<}{}^{C(CH_2Ph)\cdot CO}_{CH{=\!=}CCl}{>}O$.

The ethereal solution from the preparation of the hydroxy-anhydride described above contains the chloro-anhydride, together with a small quantity of dissolved hydroxy-anhydride. Separation can be effected by shaking the ethereal solution with dilute aqueous sodium hydrogen carbonate until the lower layer is alkaline. It is necessary to use the alkali dilute, because otherwise the separation of the sodium salt of the hydroxy-pyrone, which like the potassium salt is insoluble in excess of the reagent, causes difficulty in separating the two layers. The deep magenta alkaline washings deposit a further quantity of the hydroxy-anhydride when acidified. The dried ethereal solution leaves an oil on evaporation, which quickly becomes solid. When recrystallised by dissolving in hot light petroleum (b. p. 60—70°), and clearing when cooled by the addition of a little chloroform, it is obtained in long, slender needles, melting at 74°:

0·1934 gave 0·1258 AgCl. Cl = 16·09.

$C_{12}H_9O_2Cl$ requires Cl = 16·09 per cent.

The chloro-anhydride is readily soluble in benzene or chloroform.

When treated with strong aqueous potassium hydroxide, heat is generated, and the anhydride slowly passes into solution. At the same time the crystalline potassium salt of the hydroxy-anhydride separates.

The cis- *and* trans-*Semianilides of the α-Monosubstituted Glutaconic Acids.*

The trans-*Semianilide of α-Methylglutaconic Acid,*
$CO_2H\cdot CH_2\cdot CH{:}CMe\cdot CO\cdot NHPh$.
—Reference has been made in the introduction (p. 2213) to a difference in the result obtained by us and by Feist and Pomme respecting the behaviour of α-methylglutaconic acid towards aniline. The semianilide is produced in quantitative yield when the *trans*-acid, mixed with one molecular proportion of aniline, is heated at 150° for ten minutes, and is isolated by rubbing the product with pure ether. It crystallises from ethyl acetate in needle clusters, which melt at 189°, and lose carbon dioxide at 195°. The semianilide is soluble in aqueous sodium carbonate:

0·2167 gave 0·5220 CO_2 and 0·1129 H_2O. C = 65·69; H = 5·80.
$C_{12}H_{13}O_3N$ requires C = 65·8; H = 5·9 per cent.

0·2000 required 33·75 c.c. NaOH solution (1 c.c. = 0·001079 gram NaOH) for complete neutralisation. $C_{12}H_{13}O_3N$ (monobasic) requires 33·86 c.c.

When the semianilide is heated until carbon dioxide has ceased to be evolved, the product is an oil insoluble in alkali. It was purified by dissolving in ether, and washing with dilute alkali. As the residue still showed no signs of solidifying and appeared to decompose on distillation, it was analysed:

0·2051 gave 0·5649 CO_2 and 0·1386 H_2O. C = 75·11; H = 7·51.
$C_{11}H_{13}ON$ requires C = 75·4; H = 7·4 per cent.

The numbers closely approximate to those required for the anilide, $CHMe{:}CMe\cdot CO\cdot NHPh$.

Oxidation of the Semianilide.—The oxidation was effected by dissolving the acid in sodium hydrogen carbonate solution and adding the calculated quantity of a solution of permanganate. The solution was then filtered, acidified, evaporated to dryness, and extracted in a Soxhlet apparatus with ether.

Malonic acid, melting at 132°, was obtained from the ethereal solution (Found, C = 34·42; H = 3·88. Calc., C = 34·6; H = 3·8 per cent.).

The trans-*Semianilide of α-Ethylglutaconic Acid,*
$CO_2H\cdot CH_2\cdot CH{:}CEt\cdot CO\cdot NHPh$.
—This substance is prepared in precisely the same manner as the

a-methyl derivative. It crystallises from dilute alcohol in needles, which melt at 170°, giving off carbon dioxide at 180°. The semianilide is soluble in aqueous sodium carbonate:

0·2096 gave 0·5137 CO_2 and 0·1181 H_2O. C = 66·84; H = 6·28.

$C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4 per cent.

The trans-*Semianilide of a-Benzylglutaconic Acid*,
$CO_2H\cdot CH_2\cdot CH{:}C(CH_2Ph)\cdot CO\cdot NHPh$.
—The preparation of this compound is the same as described in the case of the a-methyl derivative. It crystallises from dilute alcohol in small needles, which melt at 175°, and evolve carbon dioxide at 190°:

0·1846 gave 0·4965 CO_2 and 0·0955 H_2O. C = 73·35; H = 5·76.

$C_{18}H_{17}O_3N$ requires C = 73·2; H = 5·8 per cent.

The *cis*-semianilides are prepared by the action of aniline on the hydroxy-anhydrides. They pass into the *trans*-semianilides when heated at 150°.

The cis-*Semianilide of a-Methylglutaconic Acid*,
$CO_2H\cdot CH_2\cdot CH{:}CMe\cdot CO\cdot NHPh$.
—When a solution of the hydroxy-anhydride of a-methylglutaconic acid in benzene is mixed with a benzene solution of the requisite quantity of aniline, heat is generated, and the solution becomes deep magenta-red. At the same time a solid substance separates, which is collected and rubbed with pure ether. The semianilide crystallises from dilute alcohol in slender needles, which melt at 148°, evolving carbon dioxide at a higher temperature:

0·1461 gave 0·3509 CO_2 and 0·0797 H_2O. C = 65·60; H = 6·08.

$C_{12}H_{13}O_3N$ requires C = 65·8; H = 5·9 per cent.

The semianilide is readily soluble in aqueous sodium carbonate. When it is heated at 150° for twenty minutes, transformation into the *trans*-semianilide is complete. The compound may be isolated by rubbing the product with ether.

The cis-*Semianilide of a-Ethylglutaconic Acid*,
$CO_2H\cdot CH_2\cdot CH{:}CEt\cdot CO\cdot NHPh$.

—Since this semianilide is soluble in benzene it does not separate when a benzene solution of the hydroxy-anhydride is mixed with a benzene solution of aniline. It may be isolated, however, by evaporating the solution free from benzene, adding ether, and shaking with aqueous sodium carbonate. The oil which separated on acidifying the alkaline solution set to a solid mass, and was purified by rubbing with dry ether and recrystallising from dilute alcohol. The product obtained in this manner did not melt sharply; it was therefore rubbed with benzene, and filtered from a small quantity

of insoluble material. The residue from the benzene filtrate was then recrystallised from dilute alcohol, and obtained in silky needles, melting at 121°:

0·1428 gave 0·3495 CO_2 and 0·0845 H_2O. C = 67·01; H = 6·59.
$C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4 per cent.

The portion insoluble in benzene proved to be the *trans*-semianilide melting at 170°, and it is therefore evident that even at the temperature of the water-bath some conversion of the *cis*- into the *trans*-modification had taken place. This change is complete when the *cis*-semianilide is heated at 150° for fifteen minutes.

The Semianilide from the Normal Anhydride of α-Ethylglutaconic Acid, $CO_2H·CH:CH·CHEt·CO·NHPh$.—This substance is prepared by the action of aniline on the normal anhydride in benzene solution, and is isolated by extracting the ethereal solution of the residue with aqueous sodium carbonate. It crystallises from dilute alcohol in small plates, melting at 149°:

0·1499 gave 0·3666 CO_2 and 0·0884 H_2O. C = 66·75; H = 6·55.
$C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4 per cent.

The cis-*Semianilide of α-Benzylglutaconic Acid*,
$CO_2H·CH_2·CH:C(CH_2Ph)·CO·NHPh$.

In this case the semianilide separates when benzene solutions of the hydroxy-anhydride and aniline are mixed. It crystallises from dilute alcohol in long, slender needles, melting at 143°. The semianilide dissolves in aqueous sodium carbonate, but if the alkali is strong an oily sodium salt is precipitated, which, however, dissolves when water is added:

0·2042 gave 0·5451 CO_2 and 0·1022 H_2O. C = 73·00; H = 5·57.
$C_{18}H_{17}O_3N$ requires C = 73·2; H = 5·8 per cent.

The *cis*-semianilide is completely converted into the *trans*-semianilide, melting at 175°, when heated at 150° for fifteen minutes.

The Normal Anhydrides, Hydroxy-anhydrides, and Chloro-anhydrides of the Disubstituted Glutaconic Acids.

αβ-Dimethylglutaconic Acid.—We have been unable to prepare the normal anhydride of this acid. The tendency for the mobile hydrogen atom to pass outside the three-carbon system is so considerable that even when dehydration is effected at low temperatures the hydroxy-anhydride is alone formed.

The Hydroxy-anhydride of αβ-Dimethylglutaconic Acid (6-*Hydroxy-3:4-dimethyl-α-pyrone*), $\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}{>}\mathrm{O}$.

This substance is formed by the action of boiling acetyl chloride on the acid, and was described in a former communication (Trans., 1905, **87**, 1696) as the normal anhydride. It is a mobile liquid which boils at 183°/25 mm. (through a misprint the boiling point was wrongly given in the original paper):

0·1629 required 38·9 c.c. of NaOH solution (1 c.c. = 0·001193 gram NaOH) for complete neutralisation. $C_7H_8O_3$ (monobasic) requires 39·0 c.c.

The hydroxy-anhydride is precipitated by adding acid to a solution of the anhydride in alkali, and the change into the alkali salt of the dibasic acid is very slow at the ordinary temperature. The acid formed is the same as that from which the anhydride was derived. The neutral solution from the above titration becomes deep purple on keeping, and it is evident that the property of forming coloured solution in this manner is characteristic of all hydroxy-anhydrides.

The Acetyl-anhydride of αβ-Dimethylglutaconic Acid (6-*Acetoxy-3:4-dimethyl-α-pyrone*), $\mathrm{CMe}{<}\begin{matrix}\mathrm{CMe{-}CO}\\ \mathrm{CH{:}C(OAc)}\end{matrix}{>}\mathrm{O}$.

It is possible to isolate this substance in a pure condition because there is no tendency whatever for the production of the chloro-anhydride when the acid is heated with acetyl chloride at the temperature of the boiling reagent. The acid is heated with a large excess of acetyl chloride for six hours on the water-bath, and the excess of the chloride is then evaporated. The neutral acetyl-anhydride is separated from the hydroxy-anhydride by dissolving the residue in ether and shaking with aqueous sodium hydrogen carbonate, and is obtained as a crystalline solid when the ethereal solution is evaporated. It crystallises from a mixture of chloroform and light petroleum (b. p. 50—60°) in long, rhombic prisms, melting at 65°:

0·2385 gave 0·5189 CO_2 and 0·1202 H_2O. C = 59·33; H = 5·60.

$C_9H_{10}O_4$ requires C = 59·3; H = 5·5 per cent.

The acetyl-anhydride is readily soluble in benzene or chloroform; it is insoluble in light petroleum. When warmed with aqueous potassium hydroxide it slowly dissolves, and a crystalline potassium salt separates if a sufficient excess of alkali is present. The solution of this salt in water when acidified yields the acid melting at 148°.

The constitution of the acetyl-anhydride was proved by the formation of acetanilide by the action of aniline. The anhydride dissolved in benzene was mixed with a benzene solution containing excess of aniline, and the mixture evaporated free from the solvent. The residue was then dissolved in ether, and shaken, first with sodium carbonate solution and then with dilute hydrochloric acid. Acetanilide (m. p. 115°) was isolated from the ethereal solution on evaporation (Found, C = 70·92; H = 6·81. Calc., C = 71·1; H = 6·7 per cent.). When the sodium carbonate washings from the above preparation were acidified, the semianilide melting at 139° (see p. 2218) is precipitated.

The Chloro-anhydride of $\alpha\beta$*-Dimethylglutaconic Acid* (6-*Chloro-3:4-dimethyl-α-pyrone*), $CMe{<}{\begin{matrix}CMe\cdot CO\\ CH:CCl\end{matrix}}{>}O$.

This substance is prepared in small amount by heating $\alpha\beta$-dimethylglutaconic acid with twice the theoretical amount of acetyl chloride in a sealed tube at 100° for ten hours, and can be isolated in the same way as the chloro-anhydrides already described. It is a liquid which distils at 133°/26 mm.:

0·2069 gave 0·1872 AgCl. Cl = 22·37.

$C_7H_7O_2Cl$ requires Cl = 22·4 per cent.

The chloro-anhydride slowly dissolves when shaken with aqueous potassium hydroxide, and the solution, when acidified and extracted by ether, yields the acid melting at 148°.

The Normal Anhydride of $\alpha\gamma$*-Dimethylglutaconic Acid*,

$$CH(H){<}{\begin{matrix}CMe\cdot CO\\ CMe\cdot CO\end{matrix}}{>}O.$$

When 5 grams of $\alpha\gamma$-dimethylglutaconic acid are heated on the water-bath with 40 c.c. of acetyl chloride, a vigorous reaction ensues, and much hydrogen chloride is evolved. The reaction ceases after thirty minutes, and the anhydride can be isolated by evaporating the chloride, dissolving the residue in ether, and shaking the ethereal solution with aqueous sodium hydrogen carbonate. The [illegible] obtained from the ethereal solution on evaporation slowly polymerises to a resin when kept in an evacuated desiccator; as, moreover, it passed into the hydroxy-anhydride (q.v.) and other products when distilled, it was analysed after it had been kept in a vacuum for two hours. The hydrogen result is therefore rather high, owing to the presence of traces of ether:

0·2290 gave 0·5042 CO_2 and 0·1241 H_2O. C = 60·05; H = 6·02.

$C_7H_8O_3$ requires C = 60·0; H = 5·7 per cent.

The anhydride is insoluble in cold aqueous sodium carbonate, but slowly dissolves on warming. The acid melting at 147° is extracted from the acidified solution by ether.

The Hydroxy-anhydride of αγ-Dimethylglutaconic Acid (6-*Hydroxy-3:5-dimethyl-α-pyrone*), $CH{<}{\substack{CMe{-}{-}CO \\ CMe{:}C(OH)}}{>}O$.

The hydroxy-anhydride is readily prepared by heating the normal anhydride at 150° for ten minutes, and can be isolated by dissolving the melted product in ether, and shaking with aqueous sodium hydrogen carbonate. The alkaline solution, if immediately acidified, precipitates the anhydride as an oil, which quickly becomes solid. It is also formed, accompanied by some chloro-anhydride, when αγ-dimethylglutaconic acid is heated with twice the theoretical amount of acetyl chloride in a sealed tube at 100° for six hours, and can be separated by the method already described. The anhydride distils at 183°/27 mm. as a mobile oil, which solidifies on cooling. It crystallises from a mixture of benzene and light petroleum (b. p. 60—70°) in glistening plates, melting at 75°:

0·2244 gave 0·4922 CO_2 and 0·1144 H_2O. C = 59·81; H = 5·66.
$C_7H_8O_3$ requires C = 60·0; H = 5·7 per cent.

The hydroxy-anhydride is readily soluble in benzene, sparingly so in ether, and practically insoluble in light petroleum. It dissolves in aqueous sodium hydrogen carbonate with effervescence, and can be partly recovered if the solution is quickly acidified, but if kept at the ordinary temperature for twenty minutes it is completely converted into the salt of the acid from which it was derived; this can be recovered by extracting the acidified solution with ether:

0·1537 required 36·7 c.c. NaOH solution (1 c.c. = 0·00119? gram NaOH) for complete neutralisation. $C_7H_8O_3$ (monobasic) requires 36·8 c.c.

The usual purple colour is developed when the neutral solution is kept.

The hydroxy-anhydride dissolves when boiled with water, and on cooling a small amount separates unaltered. It is, however, rapidly converted by hot water into αγ-dimethylglutaconic acid.

The Chloro-anhydride of αγ-Dimethylglutaconic Acid (6-*Chloro-3:5-dimethyl-α-pyrone*), $CH{<}{\substack{CMe{-}CO \\ CMe{:}CCl}}{>}O$.

A compound to which the above formula was assigned was prepared by Feist and Reuter (*Annalen*, 1909, **370**, 82) by the action of phosphorus pentachloride on αγ-dimethylglutaconic acid

but only in very small quantity. It can be prepared in a yield of about 30 per cent. by heating $\alpha\gamma$-dimethylglutaconic acid with twice the theoretical quantity of acetyl chloride in a sealed tube at 100° for eight hours, and can be isolated in the usual manner. The compound melts at 82—83°, as described by Feist and Reuter. (Found, Cl = 22·31. Calc., Cl = 22·4 per cent.)

The chloro-anhydride slowly dissolves when warmed with aqueous potassium hydroxide, and the solution when acidified and extracted with ether yields $\alpha\gamma$-dimethylglutaconic acid, melting at 147°.

The Semianilides, Hydroxy-anils, and Anils of the Disubstituted Glutaconic Acids.

The Semianilide of $\alpha\beta$-Dimethylglutaconic Acid, $CO_2H\cdot CMe{:}CMe\cdot CH_2\cdot CO\cdot NHPh$.—This substance, which melts at 139°, was described in a former paper (Trans., 1905, **87**, 1697). When heated at 150° it loses water, and is converted into the hydroxy-anil. The same semianilide is formed from the anhydride, both before and after distillation.

The Hydroxy-anil of $\alpha\beta$-Dimethylglutaconic Acid (3-Hydroxy-2-phenyl-5 : 6-dimethyl-1 : 2-dihydropyridone),

$$\mathrm{CMe}<\begin{matrix}\mathrm{CMe{-\!\!-}CO}\\ \mathrm{CH{:}C(OH)}\end{matrix}>\mathrm{NPh}.$$

This compound can be prepared either by heating the semianilide in the manner described above, or by heating $\alpha\beta$-dimethylglutaconic acid with one molecular quantity of aniline at 150° for fifteen minutes. In both cases the product is isolated by rubbing with pure ether, in which the hydroxy-anil is insoluble. It crystallises from alcohol in lustrous plates, melting at 125°:

0·1281 gave 0·3391 CO_2 and 0·0707 H_2O. C = 72·25; H = 6·15.
0·1276 „ 0·3383 CO_2 „ 0·0675 H_2O. C = 72·30; H = 5·90.
$C_{13}H_{13}O_2N$ requires C = 72·6; H = 6·1 per cent.

0·2087 required 36·5 c.c. of NaOH solution (1 c.c. = 0·001072 gram NaOH). $C_{13}H_{13}O_2N$ (monobasic) requires 36·3 c.c.

The dissociation of the salt of the hydroxy-anil (see p. 2220) causes the neutral solution to become alkaline on keeping, but the further addition of 0·2 c.c. of $N/10$-acid is sufficient to stop this process, and therefore the amount of anil formed is too small to be isolated. The neutral solution of the alkali salt can be boiled for some considerable time without undergoing change, and it is therefore evident that the condition having the mobile hydrogen atom outside the three-carbon system possesses remarkable stability.

The Semianilide of αγ-*Dimethylglutaconic Acid*,
$CO_2H\cdot CMe\colon CH\cdot CHMe\cdot CO\cdot NHPh$.

—This compound can be prepared either from the normal anhydride or the hydroxy-anhydride by dissolving in benzene and adding a benzene solution containing rather more than the requisite amount of aniline. It can be isolated by evaporating free from the solvent, dissolving in ether, and shaking the ethereal solution with aqueous sodium carbonate. The semianilide separates from dilute alcohol in microscopic needle clusters, melting at 165—166°:

0·1883 gave 0·4604 CO_2 and 0·1130 H_2O. C = 66·68; H = 6·6[illegible].
$C_{13}H_{15}O_3N$ requires C = 66·9; H = 6·4 per cent.

When the semianilide is prepared from the hydroxy-anhydride some neutral substance remains in the ethereal solution, which crystallises from alcohol in small needles, melting at 195°, and is probably the *anilide* of αγ-*dimethylglutaconic acid*,
$NHPh\cdot CO\cdot CMe\colon CH\cdot CHMe\cdot CO\cdot NHPh$:

0·2297 gave 0·6215 CO_2 and 0·1337 H_2O. C = 73·77; H = 6·49.
$C_{19}H_{20}O_2N_2$ requires C = 74·0; H = 6·5 per cent.

When the semianilide is heated at 150° for fifteen minutes it is completely transformed into the hydroxy-anil and water.

The Hydroxy-anil of αγ-*Dimethylglutaconic Acid* (3-*Hydroxy*-2-*phenyl*-4 : 6-*dimethyl*-1 : 2-*dihydropyridone*),

$$CH{<}\begin{matrix}CMe\text{———}CO\\ CMe\colon C(OH)\end{matrix}{>}NPh.$$

After several experiments on the action of aniline on αγ-dimethylglutaconic acid it was found that the best yield of the hydroxy-anil was obtained by boiling the acid with excess of aniline for one hour. The product can be isolated by pouring the aniline solution into dilute hydrochloric acid, extracting the insoluble oil by ether, and shaking the ethereal solution with aqueous sodium carbonate.* It crystallises from dilute alcohol in plates, melting at 112°:

0·2046 gave 0·5425 CO_2 and 0·1107 H_2O. C = 72·32; H = 6·03.
$C_{13}H_{13}O_2N$ requires C = 72·6; H = 6·1 per cent.

0·1935 required 33·4 c.c. of NaOH solution (1 c.c. = 0·001072 gram NaOH) for neutralisation. $C_{13}H_{13}O_2N$ (monobasic) requires 33·6 c.c.

The indicator colour of the neutral solution (phenolphthalein) slowly returns on keeping, and it is possible to add 2·3 c.c. of $N/10$-acid before this process ceases. By using larger quantities the crystalline precipitate which separates from the neutral solution a

* A small quantity of the normal anil is always formed by this method, but is removed on crystallisation.

keeping can be collected. It crystallises from alcohol, in which it is sparingly soluble, in small needles, melting at 174°, forming a magenta-red liquid:

0·2025 gave 0·5381 CO_2 and 0·1096 H_2O. C = 72·48; H = 6·02.
$C_{13}H_{13}O_3N$ requires C = 72·6; H = 6·1 per cent.

The compound is therefore the *anil* of *αγ-dimethylglutaconic acid*, $CH(H)<^{CMe\cdot CO}_{CMe\cdot CO}>NPh$. When a neutral solution of the hydroxy-anil is acidified, the substance is precipitated unaltered, but if the neutral solution is warmed on the water-bath for half an hour and then acidified, the semianilide melting at 165—166° is precipitated. The following analysis and titration was made of this product in order to place its identity beyond question. (Found, C = 66·67; H = 6·34. Calc., C = 66·9; H = 6·5 per cent.):

0·2004 required 31·9 c.c. of NaOH solution (1 c.c. = 0·001079 gram NaOH) for neutralisation. $C_{13}H_{15}O_3N$ requires 31·88 c.c.

The colour of the indicator does not return when the neutral solution is kept. The semianilide is reconverted into the hydroxy-anil when heated at 150°.

The Normal Anhydrides and Hydroxy-anhydrides of the Trisubstituted Glutaconic Acids.

The only acid belonging to this series which we have as yet investigated is αβγ-trimethylglutaconic acid. (For method of preparation compare Trans., 1905, **87**, 1704.)

The Normal Anhydride of αβγ-Trimethylglutaconic Acid,

$$CMe(H)<^{CMe\cdot CO}_{CMe\cdot CO}>O.$$

This substance can be prepared by heating the acid with excess of acetyl chloride on the water-bath for one hour, and can be isolated by evaporating the reagent, dissolving the residue in ether, and extracting acid impurities by shaking with aqueous sodium hydrogen carbonate. It is a liquid which passes into the hydroxy-anhydride on distillation. It does not, however, show any tendency to polymerise, and can therefore be purified by placing in an evacuated desiccator for twelve hours:

0·1992 gave 0·4556 CO_2 and 0·1222 H_2O. C = 62·38; H = 6·81.
$C_8H_{10}O_3$ requires C = 62·3; H = 6·5 per cent.

The high content of hydrogen can be accounted for by the presence of traces of dissolved ether.

The Hydroxy-anhydride of αβγ-Trimethylglutaconic Acid (6-Hydroxy-3:4:5-trimethyl-α-pyrone),

$$CMe{<}\begin{matrix}CMe\text{——}CO\\CMe{:}C(OH)\end{matrix}{>}O.$$

This compound was described as the normal anhydride in the previous paper (Trans., 1905, **87**, 1705). It can be prepared either by the method then given or by heating the normal anhydride at 150° for fifteen minutes. The melting point is 119°, as stated previously. The anhydride is fairly stable in the presence of excess of alkali, but is best titrated directly with alkali in very cold dilute alcoholic solution. The figures are, however, only approximate:

0·1897 required 41·6 c.c. of NaOH solution (1 c.c. = 0·001176 gram NaOH) for neutralisation. $C_8H_{10}O_3$ (monobasic) requires 41·07 c.c.

When the hydroxy-anhydride is dissolved in alkali, no precipitate of unchanged material occurs on the addition of acid, and it is evident that even at the ordinary temperature transformation into the salt of the dibasic acid is fairly rapid. The acid formed either directly or in the presence of casein in accordance with Feist's method is the same acid as that from which the anhydride was derived.

The formation of the chloro-anhydride by the prolonged action of acetyl chloride on αβγ-trimethylglutaconic acid was not observed.

The Semianilide and Hydroxy-anil of the Trisubstituted Glutaconic Acid.

The Semianilide of αβγ-Trimethylglutaconic Acid, $CO_2H\cdot CMe{:}CMe\cdot CHMe\cdot CO\cdot NHPh$.—The same semianilide is prepared both from the normal anhydride and hydroxy-anhydride when they are treated in benzene solution with the requisite amount of aniline dissolved in the same solvent. The product is isolated by evaporating the solvent, and shaking the ethereal solution of the residue with aqueous sodium carbonate. It crystallises from dilute alcohol in slender needles, melting at 151°:

0·2100 gave 0·5223 CO_2 and 0·1317 H_2O. C = 67·83; H = 6·97.

$C_{14}H_{17}O_3N$ requires C = 68·0; H = 6·9 per cent.

The semianilide is completely converted into the hydroxy-anil when heated at 150° for fifteen minutes. It is readily soluble in benzene or alcohol.

The Hydroxy-anil of αβγ-Trimethylglutaconic Acid (3-Hydroxy-2-phenyl-4 : 5 : 6-trimethyl-1 : 2-dihydropyridone),

$$CMe{<}{\begin{matrix}CMe\text{——}CO\\CMe{:}C(OH)\end{matrix}}{>}NPh.$$

This compound is best prepared by heating the acid with one molecular quantity of aniline for fifteen minutes at 150°. The product is completely soluble in ether, and therefore the hydroxy-anil must be isolated by shaking the ethereal solution with aqueous sodium carbonate. It crystallises from dilute alcohol in small needles, melting at 103°:

0·1435 gave 0·3834 CO_2 and 0·0824 H_2O. C = 73·04; H = 6·40.
$C_{14}H_{15}O_2N$ requires C = 73·4; H = 6·6 per cent.

In this experiment the sodium carbonate extract must be acidified immediately, otherwise some semianilide is formed. The following titration was made by dissolving the hydroxy-anil in dilute alcohol, and titrating direct with alkali:

0·1621 required 24·0 c.c. NaOH solution (1 c.c. = 0·001174 gram NaOH) for neutralisation. $C_{14}H_{15}O_2N$ requires 24·1 c.c.

When the neutral solution is warmed and then acidified, the semianilide melting at 151° is precipitated on acidifying.

When the hydroxy-anil is dissolved in excess of cold alkali and the solution is titrated with standard acid until neutral, the colour of the indicator (phenolphthalein) returns on keeping. A small amount of crystalline material is obtained by adding acid until the solution remains neutral. This is the *anil* of *αβγ-trimethylglutaconic acid*, $CMe(H){<}{\begin{matrix}CMe{\cdot}CO\\CMe{\cdot}CO\end{matrix}}{>}NPh$, and separates from alcohol in slender needles, melting at 162°:

0·1562 gave 0·4186 CO_2 and 0·0906 H_2O. C = 73·08; H = 6·38.
$C_{14}H_{15}O_2N$ requires C = 73·4; H = 6·6 per cent.

The amount of the anil formed in this manner is very small, as the greater portion of the hydroxy-anil is converted into the semianilide during the course of the experiment.

The Sorby Research Laboratory,
The University, Sheffield.

CCXLIX.—*Electromotive Forces in Alcohol. Part II. The Hydrogen Electrode in Alcohol and the Influence of Water on its Electromotive Force.*

By Robert Taylor Hardman and Arthur Lapworth.

It is generally stated that the electromotive force obtained when two platinum sheets saturated with hydrogen are immersed in two dilute aqueous solutions, which are in mutual contact, is given by the expression:

$$E = \frac{RT}{F}\log_e\frac{C}{C'},$$

(where C and C' represent the concentrations of the "hydrogen ions" in the two liquids respectively, and E, R, T, and F have their usual significance), provided that there is no potential difference at the liquid boundary, and that there is no substance present which can be reduced by the hydrogen under the experimental conditions.

The quantities C and C' in the foregoing expression properly refer to those hydrions which are characteristic of aqueous solutions of acids rather than to the "free" hydrogen ions. Nevertheless, the equation is equally true in either sense, as in any given basic solvent the active mass of the latter is nearly constant, and consequently the ratio:

[solvated hydrions]/[free hydrions]

is constant for univalent ions at any fixed temperature. In such cases as the above relations hold, it is also true that:

availability of acid/[solvated hydrions]

is a constant; hence the electromotive force of the concentration cell is also given by:

$$E = \frac{RT}{F}\log_e\frac{P}{P'},$$

where P and P' are the availabilities of the acid in the two liquids (Trans., 1908, **93**, 2203, and 1910, **97**, 21).

As all the foregoing relations have a sound thermodynamic basis, the question whether "free" hydrogen ions actually exist in such solutions is immaterial at least when passing from the first expression for E to the second, the sole assumptions made being that the gas laws are applicable to the ions, and that the current production is conceived as taking place in a truly reversible manner. The supposition that the elementary hydrogen at the electrodes passes into solution as "free" hydrogen ions is not a necessary part of the

proof, as the same result is obtained if it be supposed that the process occurring at the electrodes is the direct formation of the solvated ions, as, for example:

$$H_2O + \frac{1}{2}H_2 \rightleftharpoons H{\cdot}H_2O^{\cdot} + \ominus,$$

when the free energy relations of these ions are similar to those usually associated with the "free" hydrogen ions. The ionic solution pressure must then be considered as due to the same reaction.

The formula which shows the connexion between the potential and the availabilities of the acid in the cell compartments is of more general applicability than the one first given, as it is not restricted to cases in which the solvent itself forms complex hydrions. As the only solvents hitherto investigated from this point of view come under the latter category, a general thermodynamic proof of the availability formula, although comparatively simple, is at present hardly necessary.

Occasion may be taken to point out that numerous experiments on alcoholic solutions of mineral acids show that the law of mass action holds as nearly true for such solutions as for aqueous ones. Consequently, the restrictions under which the foregoing formulæ are applied are not here appreciably more serious with the one solvent than with the other.

It has already been shown that the anticatalytic effect of water on solutions of mineral acids in organic solvents can readily be accounted for on the view that water behaves as a weak base, so that when it is added to such solutions the concentration of the "free" hydrogen ions is diminished, or the availability of the acid is depressed, and experimental proof of a direct connexion between the catalytic activity and the salt-forming power of hydrogen chloride in alcohol was adduced. In experiments described in the present paper the theory has been put to a further test by ascertaining the electromotive forces obtained with concentration cells containing alcoholic hydrogen chloride as cell liquid, and having electrodes reversible to hydrogen ions.

Preliminary experiments were made with solutions of hydrogen chloride without any subsidiary electrolyte to minimise the potential differences at the liquid boundary, and it was found that with suitable precautions consistent electromotive forces were registered which could be reproduced within less than a millivolt.

The results with solutions having different concentrations of acid in the two compartments were in fairly good agreement with the high value for the transport number of chloridion deduced by other means (Lapworth and Partington, this vol., p. 1420), when neither solution had a concentration of hydrogen chloride much less than $N/10$. With solutions of concentrations considerably less than

$N/10$, consistent and reproducible electromotive forces were again obtained, but these were almost invariably smaller than those anticipated, by several millivolts, and although various explanations suggest themselves, these cannot at present be tested; additional experiments will be undertaken in the hope of explaining this discrepancy.

Having convinced themselves that sharp and consistent results could be obtained with anhydrous alcoholic solutions, the authors then proceeded to examine what was the effect of the addition of small quantities of pure water to either solution, and observed that when the addition was made to the stronger solution a fall in the electromotive force occurred, whilst if it was made to the weaker solution an increase in the electromotive force occurred.

Quantitative experiments were then carried out, in most cases with solutions of equal concentrations of hydrogen chloride in both cells and with varying quantities of water in one cell only. The influence of small quantities of water was more marked the lower the concentration of acid, an effect which at least in part may be explained by the fact that the active mass of the free water is naturally less in the stronger solutions, as a more considerable part of that which has been added is removed by combination with the hydrogen chloride. With the highly dilute solutions observations were made only with great difficulty, as was to be expected, but with frequent repetition fairly satisfactory records were made.

In these cases any exact interpretation of the results is somewhat difficult, if not impossible, owing to uncertainties in estimating the potential of the liquid boundary. It may be regarded as safe to assume that this is in most cases of relatively small magnitude. The results of Baly, Burke, and Marsden (Trans., 1909, **95**, 1100) show that such small quantities of water affect the degree of dissociation of alcoholic hydrogen chloride to but a relatively small extent, and the same statement applies to the molecular conductivity of such solutions, so that the boundary potential resulting from the interdiffusion of the ions in the two liquids can have only a secondary importance.

The most satisfactory results of all, however, were obtained with highly dilute solutions of hydrogen chloride in presence of lithium chloride as a subsidiary electrolyte. It was found that if the two cells were filled with an alcoholic solution of this salt, and small quantities of water were added to one of the cells, no definite potential difference could be detected when the apparatus was working in the usual manner. In presence of very dilute hydrogen chloride, however, very considerable electromotive forces were registered, which were easily measured, constant and reproducible.

With the more highly dilute solutions of acid the fall in availability due to the addition of water was in close accordance with the formula:

$$\frac{P'}{P} = \frac{r}{r+w}$$

where P' is the availability of the acid in the moist solution, P that of the acid in anhydrous alcohol, w being the concentration of the water in gram-molecules per litre, and r a constant (compare Trans., 1910, **97**, 22). On calculating r by means of this formula for the separate observations, it was found to decrease rapidly with the amount of water present in the stronger solutions, less rapidly with the weaker ones, and always approaching a value 0·122, which was reached with $N/500$-hydrogen chloride in presence of lithium chloride.

It has been shown in previous papers already referred to, that the availability of this acid as measured by its activity in accelerating the esterification of an acid, or by its power of forming salts with a weak base, may be represented by a formula identical with the above, the value of r approximating to 0·1 at 25° (compare, in particular, Trans., 1910, **97**, 22 *et seq.*). Goldschmidt and Udby, on the other hand, obtained results from measurements of the velocity of the esterification of numerous acids, indicating that the speed is proportional to $1/r+w$ if the value 0·15 be assigned to r (*Zeitsch. physikal. Chem.*, 1907, **60**, 735 *et seq.*), so that the discrepancies between results obtained by entirely different methods are not greater than those between values deduced by different observers when using the same method. The relatively small magnitude of the divergence will be clear when it is realised that the presence of less than one-tenth per cent. of water in the alcohol would be sufficient to cause a variation of the same magnitude as is seen in the extreme values hitherto assigned to r at 25°, although it is highly improbable that this is the origin of the discrepancies, which may perhaps be traced when more refined methods have been developed.

The results so far obtained appear to offer unequivocal support for the solvate theory for highly ionised acids, and the expression:

$$(C_2H_6O,H)^{\cdot} + H_2O = (H_2O,H)^{\cdot} + C_2H_6O,$$

put forward for the first time by Goldschmidt and Udby as the basis of an explanation of the depressant effect of water on the catalytic activity of acids in promoting esterification, may, if interpreted broadly, be regarded as representing the equilibrium in a highly dilute solution of an acid in moist alcohol. Applied with this reservation and solely to those cases of catalysis and salt formation known to be due exclusively, or nearly so, to reactions

of complex hydrions, the solvate theory renders unnecessary, at least for the present, theories such as that of Reid (*Amer. Chem. J.* 1909, **41**, 499 *et seq.*), where changes in the viscosity of the medium are suggested as one of the principal causes of the anticatalytic influence of water on organic media.

The results of Tubant and his colleagues, obtained by measurements of the speed of inversion of menthone by acids in alcoholic solution (*Annalen*, 1910, **377**, 284 *et seq.*), suggest that this reaction is not so nearly exclusively ionic in character as is ordinary accelerated esterification, for the velocities of reaction are not even roughly proportional to the "hydrogen ion" concentration in absolute alcohol as measured by the degree of ionisation of the catalyst. It is therefore not surprising that the influence of water on the reaction appears anomalous when contrasted with the cases dealt with in the present paper.

EXPERIMENTAL.

The apparatus employed for measuring the electromotive forces was that used during the experiments described in Part I. (this vol., p. 1420). The anhydrous alcohol and solutions of hydrogen chloride were prepared as on the former occasion.

The cells used were a pair, each of which was a simple modification of a type in common use, but were joined by means of a narrow glass U-tube. Each cell was provided with a raised reservoir of the solution and with suitable taps, by means of which the levels of the liquids in the cells could readily be adjusted or contact between the cell liquids secured.*

Readings were made by first opening three of the four taps separating the two cells; usually there was enough leakage through the fourth to allow of an approximate estimate of the potential, which could therefore be nearly balanced before this stopcock was opened to obtain a more exact reading. Even after many measurements had been made, involving opening all four taps, the potential varied but imperceptibly, and in no case where numbers are given without comment was there any evidence that a variation in potential had been caused by mixing of the solutions.

Before each experiment the cells and U-tube were carefully cleaned, washed with pure anhydrous alcohol, and dried at 100°.

* The more convenient method usually employed in working with the hydrogen electrode is to use one cell in combination with a calomel electrode; thus, Denham (Trans., 1908, **93**, 41) was able to obtain very satisfactory results with aqueous solutions of salts of weak bases, employing such a combination. In the case of alcoholic solutions of hydrogen chloride, however, the calomel electrode has not given such sharp results as the hydrogen electrode, so that it was thought desirable to avoid its use in the present series of measurements.

All measurements were made at $25° \pm 0.05$.

In preliminary experiments very unsatisfactory results were obtained, both with electrodes of platinum foil and with others made of platinum films deposited on glass; this was finally found to be due almost wholly to the condition of the platinum surfaces. Constant electromotive forces and consistent results were obtained with platinum plates only when these had been heated to redness, platinised in the usual manner, and washed repeatedly, first with water and then with absolute alcohol, and transferred at once, while still moist, to the cells. At the moment before the insertion of the electrodes the whole of the remainder of the apparatus should otherwise be in full working order, and a fairly rapid stream of hydrogen should have been passing for a sufficiently long time to insure the complete expulsion of all other gases from the vessels, tubes, and solutions. The electrodes should not be used twice, but require cleaning with boiling nitric acid, replatinising, and treating as above before each new experiment.

Electrodes of platinised glass, if newly prepared, coated with platinum black, washed as above and used at once, also gave excellent results, identical with those obtained with the foil-electrodes, but as it was necessary after each experiment to renew the main films and they offered no advantages as compared with the other type of electrodes, their use was discontinued.

When the apparatus was working in a satisfactory manner it was observed that a nearly steady electromotive force was obtained in one or two minutes after the electrodes had been inserted, and when this was not the case, experience showed that it was useless to continue the experiment; if the cells were short-circuited with open taps for several seconds and the circuit then broken, the original potential was attained once more in less than a minute.

Results.

Measurements made during some typical experiments at 25° are given below. In each of the cases which follow immediately, the solutions used in the two cells were prepared from the same specimen of alcohol.

The time is given in hours after the observations were began, usually within two minutes of the insertion of the electrodes. The potentials given are the means of several readings in each case.

The arrows indicate the direction of the positive current inside the cells.

The observations in the two experiments which follow immediately are given to show the influence of time on the potentials observed.

They were chosen at random from a large number of similar records.

(1) *With Slightly Moist Alcohol as Solvent (Commercial Absolute).*

H_2,1·114N-HCl | 0·1021N-HCl,H_2.
←

Time.	Potential.	Time.	Potential.
0·0 hour	0·0447 volt	1·75 hours	0·0467 volt *
0·5 ,,	0·0447 ,,	2·5 ,,	0·0467 ,,
1·0 ,,	0·0467 ,,	3·25 ,,	0·0467 ,,

* Although the accuracy of the potentials is not guaranteed within much less than a millivolt, individual readings could be compared within 0·2—0·3 millivolt. For the sake of comparisons the calculated means are given in all cases to 0·1 millivolt.

[With cells reversible to chloridion and prepared with the same two solutions, the potential obtained was 0·060 volt at the same temperature.]

(2) *With Alcohol dried over Calcium.*

H_2,0·6341N-HCl | 0·06408N-HCl,H_2.
←

Time.	Potential.	Time.	Potential.
0·0 hour	0·0291 volt	1·5 hours	0·0283 volt
0·66 ,,	0·0283 ,,	4·0 ,,	0·0289 ,,
0·91 ,,	0·0283 ,,		

The slight rise indicated in the last reading was perhaps due to a slight mixing of the solutions during the considerable time occupied by the experiment.

A number of comparative experiments were made in the early part of the investigation with different electrodes. In all cases where the alcohol was moist a sensibly constant potential was reached within fifteen minutes; thus with solutions of hydrogen chloride in two different concentrations in the cells with 99·7 per cent. alcohol as solvent, tests with seven different electrodes gave potentials between 0·0424 and 0·0490 volt. On the other hand, with solutions prepared from calcium-dried alcohol, constant values of the potentials were obtained almost as soon as it was possible to begin making measurements; thus with 0·6341N-hydrogen chloride and 0·06408N-hydrogen chloride respectively in absolute alcohol, five different pairs of electrodes of platinised foil gave potentials identical with one another within the limits of the bridge-readings, namely, 0·0282 ± 0·0003 volt. This value is in close agreement with that required, namely, 0·02806 volt if the transport number $(1-n)$ of the chloridion in the solutions is taken as 0·32, which is nearly that deduced by other methods (compare this vol., p. 1420).

Other experiments were made with solutions of hydrogen chloride with concentrations considerably lower than the above; thus the arrangement:

$$H_2,0{\cdot}100N\text{-}HCl \,|\, \underleftarrow{0{\cdot}010N}\text{-}HCl,H_2$$

gave a potential of 0·0214 volt, or some seven millivolts less than that obtained for the stronger solutions having much the same total concentration ratio. Other measurements with several different samples of alcohol have shown that when either cell contains a solution having a concentration of hydrogen chloride less than about $N/20$, the potential differences, although steady and reproducible with considerable accuracy, are invariably smaller than those calculated with the above formula by several millivolts. The explanation which first suggests itself, namely, that the value used for the transport number of chloridion in alcohol is too low, or variable, must, in the authors' opinion, be rejected; further, the presence of a constant small quantity of water or other impurity more basic than alcohol would have an influence in the opposite sense from that observed. Pending further investigation, this record of the general nature of these results is the only contribution which need be made at the present time.

The unexpected sharpness of the potentials and the accuracy with which they are reproduced led the authors to proceed at once to the main object they had in view, namely, to investigate the effect of water on the potential of the hydrogen electrode in alcohol, with the results recorded in the following section.

The Influence of Small Quantities of Water on the Potential of the Hydrogen Electrode in Alcoholic Hydrogen Chloride.

The experiments on this aspect of the subject were carried out in much the same manner as those above described. In most cases the contents of one of the cells were quite dry, whilst those of the other contained a known concentration of water.

In the experiments *c*, *d*, *e*, *f*, the total concentration of the hydrogen chloride in the two cells was the same, but varying quantities of water were present in one cell liquid only. The direction of the positive current in the cells was always from the moist solution to the anhydrous one.

In one column are given the values of P'/P calculated by means of the formula (5):

$$E = \frac{RT}{F}\log_e\frac{P}{P'}.$$

These represent the apparent relative values of the concentrations of the free hydrogen ions, or the apparent relative values of the

availability of the acid, in the moist as compared with the anhydrous solution. Cases *b* and *c* approach most nearly the ideal state of low concentration, *c* representing the most dilute solution of hydrogen chloride with which sharp readings could be taken, and *b* the case where still more dilute acid was used with a subsidiary electrolyte.

The values of *r*, the apparent "water-value" of alcohol at 25°, were calculated by means of the formula (Trans., 1910, **97**, 22):

$$P' = Pr/r + w,$$

where P' is the availability of the acid in the moist solution, P that of the acid in the anhydrous solution, and *w* represents the number of gram-molecules of water present in one litre of the moist solution.

The numbers given under (*b*) represent the means of three sets of results, concordant within two millivolts, obtained with three samples of $N/500$-hydrogen chloride in alcohol in presence of an equal concentration of purified lithium chloride ($N/10$) in both cells. Readings were sharp, and were easily made.

(*b*) 0·002N-HCl *and* 0·100N-LiCl *in both cells;* varying quantities of water in the second cell.

Potential.	*w*.	P'/P.	*r*.
0·0384 volt	0·444	0·224	0·128
0·0467 ,,	0·666	0·163	0·129
0·0590 ,,	1·00	0·108	0·122

In case (*c*) readings were also fairly sharp, but in absence of a subsidiary electrolyte measurements were very difficult with solutions less concentrated than $N/100$.

(*c*) 0·01N-HCl *in both cells;* water in one cell only.

Potential.	*w*.	P'/P.	*r*.
0·0420 volt	0·555	0·195	0·135
0·0551 ,,	1·00	0·117	0·132

(*d*) 0·020N-HCl *in both cells;* water in one cell only.

Potential.	*w*.	P'/P.	*r*.
0·0187 volt	0·222	0·48	0·205
0·0298 ,,	0·444	0·31	0·199
0·0400 ,,	0·666	0·20	0·166
0·0476 ,,	0·888	0·156	0·164
0·0515 ,,	1·00	0·134	0·155

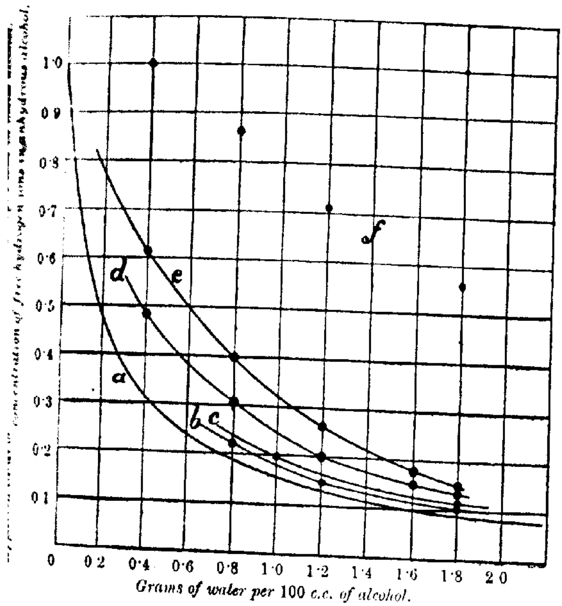
(*e*) 0·0853*N*-HCl *in both cells;* water in one cell only.

Potential.	*w*.	*P'*/*P*.	*r*.
0·0125 volt	0·222	0·62	0·363
0·0237 ,,	0·444	0·40	0·296
0·0347 ,,	0·666	0·26	0·234
0·0440 ,,	0·888	0·18	0·195
0·0484 ,,	1·00	0·152	0·179

(*f*) 0·8446*N*-HCl *in both cells;* water in one cell only.

Potential.	*w*.	*P'*/*P*.	*r*.
0·0000 volt	0·224	1·0	
0·0040 ,,	0·444	0·86	2·74
0·0090 ,,	0·666	0·71	1·63
0·0140 ,,	1·00	0·57	1·33

In the diagram the results of the latter part of the investigation are expressed graphically, and the apparent values of *P'*/*P*, or the



ative concentrations of the free hydrogen ions, are indicated in curves *b*—*f* corresponding with the experiments indicated with se letters.

The curve (*a*) is that deduced from measurements of the effect water on the catalytic activity of very dilute hydrogen chloride

7 H 2

in alcohol, adopting 0·1 as the most probable value of r. The curve representing the results of Goldschmidt and Udby on esterification lies just above c, and its separate insertion on the diagram was hardly possible. Similarly, the results obtained from measurements of the salt-forming power of extremely dilute hydrogen chloride in alcohol is nearly coincident with a and slightly below it. Generally speaking, the more dilute the acid with which the experiments are made the lower the position of the curve on the diagram.

Attention may be drawn to the fact that any tendency for lithium chloride to withdraw part of the water from alcoholic solutions would have the result of raising b towards or above c, but a further result would be a decrease in the apparent value of r with increase in the concentration of water, and there is little evidence of this in the experiments made so far. The value of r in presence of lithium chloride requires determination by other methods, and experiments on the point will be undertaken.

Conclusions.

The solvate theory of acids indicates that, in highly dilute moist alcoholic solution the concentration of the free hydrogen ions from a mineral acid may be represented by the expression:

$$[H] = [H_0]\frac{r}{r+w}.$$

where $[H_0]$ is the concentration of "free" hydrogen ions in the anhydrous solution, w is the concentration of water in gram-molecules per litre, and r is the "water-value" of the alcohol at the temperature referred to.

If the conception of "free" hydrogen ions is discarded in the absence of any direct proof of their existence, the law may be expressed in terms of the availability, P, of the acid, thus:

$$P = P_0\frac{r}{r+w},$$

where P_0 is the availability of the acid in anhydrous solution.

Experiments on three entirely independent lines confirm the general applicability of the above formula, and the only discrepancy concerns the precise value of r at 25°; this discrepancy is probably due, however, to the small magnitude of r, and the consequent difficulties in fully eliminating all sources of experimental error, especially as with low concentrations of acid the solutions are very sensitive to certain impurities.

The following estimates of the value of r at 25° have now been made:

A. *By Measurements of Esterification Velocities* (Catalysis).

(i) $r = 0{\cdot}15$ (Goldschmidt and Udby).

(ii) $r = 0{\cdot}10$—$0{\cdot}11$ (Lapworth and Partington).

(iii) $r = 0{\cdot}09$—$0{\cdot}095$ (Jones and Lapworth).

B. *By Measurements of Salt-forming Power* (Availability).

(iv) $r = 0{\cdot}089$—$0{\cdot}108$ (Lapworth and Partington).

(v) $r = 0{\cdot}095$ (Jones and Lapworth).

C. *By the* E.M.F. *of the Hydrogen Electrode* (Concentration of free $H^{\cdot}$ ions).

(vi) $r = 0{\cdot}127$ (Hardman and Lapworth).

Having regard to the numerous sources of error, the numbers given in this communication are only quoted as being approximately correct, and many of the more important ones will be redetermined, with such additional precautions as may suggest themselves; the inquiry into electromotive forces and equilibria in alcohol and other organic media will be extended along lines similar to those suggested in this and previous papers.

Part of the expense of this investigation was defrayed by a grant from the Government Grant Research Fund of the Royal Society, for which the authors desire to express their indebtedness.

SCHUNCK LABORATORY,
UNIVERSITY OF MANCHESTER.

CCL.—*Polymorphic Phthalylhydrazides.*

By FREDERICK DANIEL CHATTAWAY and DONALD FREDERICK SANDYS WÜNSCH.

SOME years ago it was observed that hot saturated solutions of phthalylphenylhydrazide almost invariably deposited crystals of two distinct forms, one orange and the other of so pale a yellow as to seem almost colourless when viewed beside the orange modification; these crystals could easily be separated by hand, and each modification could be obtained in a pure state free from the other by allowing crystallisation to take place at a suitable temperature. Dunlap (*J. Amer. Chem. Soc.*, 1905, **27**, 1091) published an account of similar observations while the work was in progress, and it was consequently discontinued.

The authors have recently resumed the subject to ascertain if this property of crystallising in two differently coloured forms is common to all the phthalylhydrazides.

So far, only one other instance has been found among the simple phthalyl derivatives, but it seems certain that this is due to the exact conditions necessary for the first appearance of the less highly coloured modification not having been realised in the remaining cases. Many observations on related compounds, which will be communicated later, lead to the conclusion that it should be possible to obtain every phthalyl- and substituted phthalyl-hydrazide in two modifications differing widely in colour and in crystalline form.

The phthalylhydrazides are very easily obtained by heating together at about 100° equivalent amounts of phthalic anhydride and the corresponding hydrazine, when water is eliminated, thus

$$C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}O + H_2N{\cdot}NHR = C_6H_4{<}\genfrac{}{}{0pt}{}{CO}{CO}{>}N{\cdot}NHR + H_2O$$

The phthalylhydrazides crystallise extremely well from all ordinary solvents. The modifications separating at the higher temperatures are orange, whilst those separating at the lower temperatures are much paler, in fact, almost colourless. In every case where only one modification has been obtained it is the one having the deep orange colour.

Instances like the foregoing, in which organic substances of the same composition exist in forms showing distinctly different properties, are very frequent.

Such diversities in the case of liquids or gases can always be referred to differences in either the size or structure of individual molecules, and can therefore be formulated according to conventional usage by different structural formulæ. But among solids of the same composition the dissimilar properties may be due either to a difference in the size or the atomic arrangement of the individual molecules, that is, to polymerism or isomerism, or to a difference in the manner in which the molecules group themselves when the substance assumes the crystalline condition—that is to polymorphism. Although differences of atomic arrangement are generally associated with marked differences in chemical behaviour whilst differences in molecular grouping only cause variations in the physical properties, it is not always easy to decide whether any given pair of substances are isomeric or polymorphic. They are usually regarded as isomeric if any differences of behaviour observed in the solid state persist when the compounds are dissolved, melted, or gasified, or if the two forms in specified reactions carried out under similar conditions yield different derivatives.

The two modifications of the phthalylhydrazides differ only in colour and crystalline shape, and the dissimilarity, so far as is known at present, disappears when the distinct solid substances are

dissolved. They must therefore provisionally be regarded as polymorphic, and not as isomeric or polymeric modifications. Since, however, the phthalylhydrazides may have the unsymmetrical configuration, the possibility that they may be stereoisomerides ought not to be lost sight of.

No differences in the chemical behaviour of the two forms have been observed; it should be noted, however, that their peculiar nature makes it impracticable to obtain derivatives which might decide the point beyond question.

The polymorphic phthalylhydrazides are enantiotropic, the two forms transforming at a definite temperature much below the melting point of either. The change in the solid state, however, takes place so slowly that it is possible for either form to exist in a more or less unstable condition at a temperature below or somewhat above the transition temperature for a limited period, depending on the rate of transformation. The transition points of the two pairs of polymorphic phthalylhydrazides described in this paper are at the present time being determined, and appear not to be very far removed from the ordinary temperature.

On heating a crystal of the colourless modification of phthalylphenylhydrazide to a temperature approaching 100°, the rate of transformation is so much increased that specks of the yellow modification almost at once appear, and grow into the mass until the whole is transformed. This conversion into the orange-coloured form takes place more easily when the white crystals are heated in a saturated alcoholic or acetic acid solution to about 60° or 70°.

Transformation of the orange-coloured phthalylphenylhydrazide into the colourless modification is so slow at the ordinary temperature that, not only may the yellow and colourless crystals be kept in contact for years without apparent change, but both forms can exist side by side for days in a saturated alcoholic solution without the orange-coloured crystals appreciably diminishing or the white crystals increasing in size.

Crystals of the pale yellow modification of phthalylphenylmethylhydrazide similarly transform quickly into the orange when heated to the neighbourhood of 100°, while the orange-coloured crystals when dry remain unchanged for months at the ordinary temperature. On the other hand, if crystals of the orange-coloured modification of phthalylphenylmethylhydrazide are placed in a saturated alcoholic solution at the ordinary temperature in presence of a crystal of the pale modification, they become completely transformed in a few hours, the orange-coloured crystals dissolving, and well-shaped crystals of the very pale yellow form taking their place.

Either form of phthalylphenylhydrazide or of phthalylphenyl-

methylhydrazide can be obtained at will by slightly superaturating a solution above or below the transition temperature and placing in it a crystal of the required modification. As, however, the difference in solubility of the two forms is at any temperature slight compared with the change of solubility as the temperature varies, a hot solution on cooling may pass into the metastable or even into the labile condition for the pale form, even when crystals of the orange form are present, so that, as might be expected, crystals of both modifications frequently separate together.

For convenience of reference the crystallographic constants of the substances described in this paper are given in the following table [1]:

Hydrazide.	Modification.	System.	Crystallographic constants.
Phthalylphenyl	Bright yellow	Monoclinic	$a : b : c = 1{\cdot}1573 : 1 :$ [illegible] $\beta = 126°26'$
Phthalylphenyl	Pale yellow	Orthorhombic	$a : b : c = 1{\cdot}0875 : 1 :$ [illegible]
Phthalyl-*p*-tolyl	Deep orange	Monoclinic	$a : b : c = 1{\cdot}7525 : 1 :$ [illegible] $\beta = 126°30'$
Phthalyl-*o*-tolyl	Bright orange	Monoclinic	$a : b : c = 0{\cdot}5555 : 1 :$ [illegible] $\beta = 96°5'$
Phthalyl-*p*-bromophenyl	Bright yellow	Monoclinic	$a : b : c = 1{\cdot}5047 : 1 :$ [illegible] $\beta = 103°7'$
Phthalyl-*p*-chlorophenyl	Bright yellow	?	?
Phthalylphenylmethyl	Bright orange	Triclinic	$a : b : c = 0{\cdot}5853 : 1 :$ [illegible] $\alpha = 110°0'$, $\beta =$ [illegible] $\gamma = 68°17'$
Phthalylphenylmethyl	Pale yellow	Monoclinic	$a : b : c = 0{\cdot}7569 : 1 :$ [illegible] $\beta = 92°10'$
Phthalylphenylbenzyl	Bright orange	Monoclinic	$a : b : c = 0{\cdot}8878 : 1 :$ [illegible] $\beta = 93°49'$
Phthalyl-α-naphthyl	Orange	?	?
Phthalyl-β-naphthyl	Orange	?	?

Phthalylphenylhydrazide, $C_6H_4<\substack{CO\\CO}>N{\cdot}NH{\cdot}C_6H_5$.

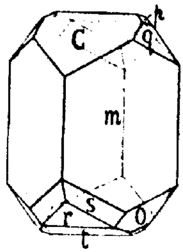
Phthalylphenylhydrazide has been described by Pickel (*Annalen*, 1886, **232**, 232), Hötte (*J. pr. Chem.*, 1886, [ii], **33**, 99; 1887, [ii], **35**, 265), Pellizzari (*Gazzetta*, 1886, **16**, 203), Just (*Ber.*, 1886, **19** 1204), Henriques (*Ber.*, 1888, **21**, 1616), and Eibner and Merkel (*Ber.*, 1902, **35**, 2300). Their descriptions of the compound do not agree, especially as regards its colour, evidently owing to one or other of the modifications only having been observed. It is best obtained by dissolving phthalic anhydride in alcohol, adding the equivalent amount of phenylhydrazine, freshly distilled and free

[1] This and all the other descriptions of the crystals given in this paper have been furnished to us by Mr. T. V. Barker, Demonstrator of Mineralogy in the University of Oxford.

from aniline, evaporating off the alcohol, and heating the yellow, solid mass remaining on a water-bath until water-vapour ceases to be given off.[1]

The bright yellow form is best obtained by dissolving as much of the compound as possible in boiling glacial acetic acid or toluene, cooling slightly, and, after adding a few specially chosen crystals of this modification, allowing the temperature to fall very slowly. This operation is most conveniently carried out by placing the carefully corked flask in a hot water-jacketed cooler, so surrounded by cotton waste that several days are required for the temperature to fall to that of the laboratory. Bright yellow, monoclinic crystals of short and compact habit then separate, invariably free from crystals of the pale-coloured modification.

FIG. 1.



Phthalylphenylhydrazide (yellow modification).

The ratios of the axes are $a:b:c = 1{\cdot}1573:1:1{\cdot}2040$; $\beta = 126°26'$. The following forms were observed: $m-\{110\}$, $c-\{001\}$, $t-\{203\}$, $r-\{\bar{1}01\}$, $q-\{011\}$, $o-\{111\}$, $s-\{\bar{2}11\}$, $p-\{\bar{1}12\}$, and $e-\{012\}$. The habit of the crystals is shown in Fig. 1, the form e being rarely observed. Following is a table of measured and calculated angles:

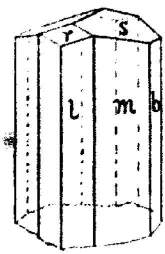
	No.	Limits.	Mean.	Calc.
$mm = 110:1\bar{1}0$	17	87°15′—87°33′	*87°20′	—
$mc = 110:001$	3	65 52 —65 59	65 56	65°51′
$mq = 110:011$	8	38 51 —39 10	*39 2	—
$cq = 001:011$	15	44 44 —44 52	*44 48	—
$ce = 001:012$	2	26 15 —26 20	26 17	26 24
$pt = \bar{1}12:\bar{2}03$	3	32 50 —33 10	32 59	33 1
$mq = 110:011$	12	78 40 —78 52	78 45	78 41
$ct = 001:\bar{2}03$	2	43 11 —43 34	43 22	43 16
$tr = \bar{2}03:\bar{1}01$	2	20 56 —21 2	20 59	21 6
$os = \bar{1}11:\bar{2}11$	4	29 26 —29 42	29 34	29 22

There is a perfect cleavage parallel to $c-\{001\}$, an imperfect one parallel to $m-\{110\}$. The optical extinction on m is straight, and an optic axis emerges obliquely through q. $D_4^{15°}$ 1·356. Molecular volume = 175·5.

The pale yellow form is best obtained by saturating toluene with the compound at about 50°, boiling for a few moments to remove all traces of crystals from the sides of the flask, and allowing to

[1] If the mass is heated much above 100° or fused, the hydrazide partly or completely decomposes according to the duration of the heating into phthalanil, ammonia, and nitrogen.

FIG. 2.



Phthalylphenylhydrazide (pale modification).

cool to about 25°. As a rule, no crystals separate. A carefully chosen fragment of the pale yellow modification is then added, and the temperature slowly allowed to fall in the cooler to that of the laboratory. The pale yellow form then separates, free from crystals of the more highly coloured form, in very faintly tinted orthorhombic plates, with $a : b : c = 1·0875 : 1 : 0·5568$. The observed forms were: $b - \{010\}$, $m - \{110\}$, $r - \{101\}$, $o - \{212\}$, $l - \{210\}$, $q - \{011\}$, $s - \{012\}$, and $n - \{230\}$. A typical crystal is shown in Fig. 2, and the observed and calculated angles follow:

		No.	Limits.	Mean.	Calc.
bn	= 010 : 230	2	31°27′—31°39′	31°33′	31 [illegible]
bm	= 010 : 110	20	42 28 —42 46	*42 36	—
ml	= 110 : 210	3	18 42 —18 49	18 46	18 [illegible]
bo	= 010 : 212	1	—	76 7	76 [illegible]
bq	= 010 : 011	2	60 51 —60 53	60 52	60 [illegible]
bs	= 010 : 012	5	74 17 —74 28	74 23	74 26
mr	= 110 : 101	6	71 59 —72 6	*72 2	—
rq	= 101 : 011	4	38 53 —39 7	39 3	38 [illegible]

There is a fairly good cleavage parallel to $b - \{010\}$. Optically the crystals clearly show their orthorhombic symmetry, the first mean line being parallel to the axis, a, with axial plane $c - \{001\}$; $2H_{Na} = ca\ 70°$, $\rho > v$. D_{4}^{15} 1·354. Molecular volume = 175·8.

The pale yellow modification when placed in a saturated solution in any solvent at about 60° rapidly dissolves and disappears, whilst deep yellow crystals separate out, so that the pale compound appears to transform into a more highly coloured one. The crystals separating often preserve to some extent the plate-like shape of the pale yellow modification, but when examined with a lens are seen to be paramorphs, consisting of small crystals of the yellow form. Determinations of the solubilities which are proceeding indicate that the transition temperature is not far above the ordinary. Transformation also takes place when the pale crystals are heated alone, but more slowly than in presence of a solvent. If large crystals of the pale form are heated to 100°, deep yellow spots quickly appear, and extend through the crystals until, after some hours' heating, the latter are transformed into opaque paramorphs of the yellow modification. This transformation is much more rapid at a higher temperature, and prevents the melting point of the pale modification being determined; even with rapid heating transformation is complete before the melting point is reached. The deep yellow modification melts at 184°. So far the transforma-

tion of the yellow into the pale modification has only been effected by dissolving the former, and allowing the pale modification to crystallise out at a comparatively low temperature. The rate of transformation at the ordinary temperature is so slow that crystals of the two forms can be left for weeks in a saturated alcoholic solution without any appreciable growth of the pale crystals. In the solid state the yellow form can be left in contact with the pale form for years at the ordinary temperature without any perceptible alteration.

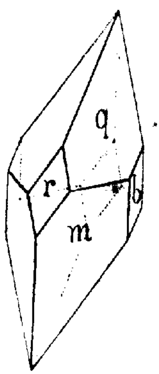
Phthalyl-p-tolylhydrazide, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>N\cdot NH\cdot C_6H_4Me$.

This substance is best prepared by dissolving equivalent amounts of phthalic anhydride and *p*-tolylhydrazine in alcohol, evaporating to dryness, and heating the solid residue on a water-bath until water-vapour is no longer given off. It is moderately readily soluble in boiling alcohol, toluene, or acetic acid, and separates in long, deep orange-yellow, prismatic crystals, which melt at 196°. The colour of this compound is very similar to that of the bright yellow modification of phthalylphenylhydrazide, but of a somewhat deeper shade. No pale modification corresponding with the second form of phthalylphenylhydrazide has yet been obtained. When crystallised from any solvent the orange modification separates, both at high and low temperatures:

0·3092 gave 29·4 c.c. N_2 (moist) at 11° and 758 mm. N = 11·25.

$C_{15}H_{12}O_2N_2$ requires N = 11·11 per cent.

FIG. 3.



Phthalyl-p-tolylhydrazide.

The crystals proved to be monoclinic with $a : b : c = 1·7525 : 1 : 0·7914$; $\beta = 126°30'$. The observed forms were: $m - \{110\}$, $q - \{011\}$, $b - \{010\}$, and $r - \{101\}$. The forms m and q predominated equally, whilst b was much smaller and r often failed. The habit is shown in Fig. 3.

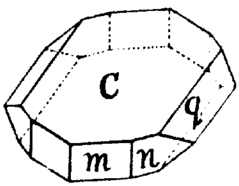
	No.	Limits.	Mean.	Calc.
bm = 010 : 110	2	35°25′—35°33′	35°29′	35°29
mm = 110 : $\bar{1}$10	4	70 36 —70 52	*70 44	—
mq = 110 : 011	7	43 12 —43 21	*43 16	—
mr = 110 : 101	3	62 10 —63 5	62 33	62 41
rq = 101 : 0$\bar{1}$1	3	35 16 —35 58	35 40	35 47
qm = 0$\bar{1}$1 : 110	9	98 19 —98 37	*98 28	—
qq = 011 : 0$\bar{1}$1	2	64 34 —64 52	64 43	64 55

There was no observable cleavage; optically the crystals are in full agreement with monoclinic symmetry; the extinction on the face m makes an angle of 29° with the edge mm. D 1·311. Molecular volume = 191·2.

Phthalyl-o-tolylhydrazide.

Phthalyl-o-tolylhydrazide was obtained exactly as the para-compound by the interaction at 1[illegible] of equivalent quantities of phthalic anhydride and o-tolylhydrazine. It is moderately readily soluble in all ordinary organic solvents, and crystallises well from hot alcohol, toluene, or glacial acetic acid in small, tabular, monoclinic crystals of a bright orange colour (compare Fig. 4), which melt at 198°. The pale modification has not yet been obtained:

FIG. 4.



Phthalyl-o-tolylhydrazide.

0·2648 gave 24·98 c.c. N_2 (moist) at 14° and 760 mm. N = 11·4

$C_{15}H_{12}O_2N_2$ requires N = 11·11 per cent.

The calculated ratios of the axes are: $a:b:c = 0·5555:1:0·749[illegible]$, $\beta = 96°5'$. The forms observed were: $c - \{001\}$, $m - \{110\}$, $n - \{120\}$, and $q - \{011\}$. The measured and calculated angles follow.

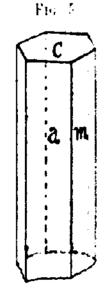
		No.	Limits.	Mean.	Calc.
qq	= 011 : 0$\bar{1}$1	3	73°13′—73°28′	73°20′	73°22′
cq	= 001 : 011	5	36 31 —36 45	*36 41	—
mq	= $\bar{1}$10 : 011	2	77 31 —77 40	77 35	77 37
mq	= 110 : 011	3	68 38 —68 47	*68 42	—
cm	= 001 : 110	2	84 40 —84 45	84 42	84 40
nm	= 120 : 110	4	18 47 —19 30	19 1	18 56
mm	= 110 : 1$\bar{1}$0	5	57 48 —57 56	*57 50	—

D_4^{13} 1·383. Molecular volume = 182·3.

Phthalyl-p-bromophenylhydrazide, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N·NH·C_6H_4Br$

The interaction of phthalic anhydride and p-bromophenylhydrazine at 100°, under conditions similar to those previously described, produces *phthalyl-p-bromophenylhydrazide*. This compound is moderately readily soluble in all ordinary organic solvents, and crystallises from hot alcohol or toluene in bright yellow, monoclinic prisms, very closely resembling in colour the yellow modification of phthalylphenylhydrazide. It melts at 206°. The pale modification has not yet been obtained:

FIG. 5.



Phthalyl-p-bromophenylhydrazide.

0·2022 gave 0·1226 AgBr. Br = 25·80.

$C_{14}H_9O_2N_2Br$ requires Br = 25·21 per cent.

The crystals are six-sided prisms of the monoclinic system (compare Fig. 5), with the axial ratios having the values $a : b : c =$ 1·047 : 1 : ? ; $\beta = 103°7'$. The only forms observed were $a - \{100\}$, $m - \{110\}$, and $c - \{001\}$, and the relative length of the vertical axis, c, could not accordingly be determined. The following angles were measured and calculated:

	No.	Limits.	Mean.	Calc.
ma = 110 : 100	5	55°34′—55°50′	55°41′	55°41′
mm = $1\bar{1}0 : 110$	6	68 35 — 68 39	*68 37	—
ca = 001 : 100	3	76 49 — 77 0	*76 53	—

There is no observable cleavage. D_4^{21} 1·682. Molecular volume = 152·5.

Phthalyl-p-chlorophenylhydrazide, $C_6H_4<\substack{CO \\ CO}>N\cdot NH\cdot C_6H_4Cl$.

Phthalyl-p-chlorophenylhydrazide was prepared as above described from *p*-chlorophenylhydrazine. It resembles the *p*-bromo-compound very closely. It crystallises from hot alcohol or toluene in bright yellow prisms, which are too slender to admit of measurement. It melts at 191°:

0·1854 gave 0·1001 AgCl. Cl = 13·35.

$C_{14}H_9O_2N_2Cl$ requires Cl = 13·01 per cent.

Phthalylphenylmethylhydrazide, $C_6H_4<\substack{CO \\ CO}>N\cdot NMePh$.

Phthalylphenylmethylhydrazide affords the best example of the dimorphism yet met with among compounds of this class, as each form can be easily obtained and transformed into the other. It is prepared exactly as the other hydrazides described in this paper by dissolving equivalent quantities of phthalic anhydride and phenylmethylhydrazine in alcohol, evaporating off the solvent, and heating the solid residue on a water-bath for some hours until water-vapour is no longer given off. The yield is practically theoretical. It is moderately soluble in all ordinary organic solvents, and crystallises well from hot solutions in toluene or alcohol. When such a solution is allowed to cool, the modification stable at the higher temperature crystallises out in long, bright orange-coloured, triclinic prisms. If these crystals are allowed to remain in the mother liquor for some days, stouter crystals of the modification stable at a lower temperature and exhibiting a very pale yellow tinge make their appearance, and grow at the expense of the orange-coloured crystals, which become etched, dissolve away, and finally disappear. At the ordinary temperature of the laboratory a few grams become completely transformed in a day or so, depending on the size of the

original crystals. The pale yellow crystals of the modification stable at the lower temperature being produced thus under ideal conditions, as the solution is always slightly supersaturated with regard to them, are especially fine in shape and appearance. When crystals of the pale form are placed in a saturated alcoholic solution at about 40°, they rapidly pass into solution, and crystals of the orange-coloured modification appear in their place. The exact transition point is being determined. When a crystal of the pale form is heated at 100°, specks of the yellow form soon appear, and grow until an opaque paramorph of the original crystal is produced, consisting of small crystals of the orange modification. This change becomes very rapid a few degrees above 100°, this being much below the melting point of the pale yellow modification, which consequently cannot be determined. The orange-coloured modification melts at 127°:

Orange Modification:—

0·3543 gave 34·2 c.c. N_2 (moist) at 15° and 758 mm. N = 11·22.

Pale Yellow Modification:—

0·2333 gave 22·5 c.c. N_2 (moist) at 15° and 758 mm. N = 11·21.

$C_{15}H_{12}O_2N_2$ requires N = 11·11 per cent.

The essential difference between the two forms is clearly brought out by the following crystallographic determination, for they crystallise in different systems.

(1) *Orange Modification.*

The crystals are triclinic, and have the following crystallographic constants: $a : b : c = 0·5853 : 1 : 0·3801$; $\alpha = 110°0'$, $\beta = 114°16'$, $\gamma = 68°17'$.

Forms: $b-\{010\}$, $a-\{100\}$, $m-\{1\bar{1}0\}$, $c-\{001\}$, $r-\{101\}$, $p-\{\bar{1}01\}$, $q-\{011\}$, and $o-\{\bar{1}\bar{1}1\}$. Two crops of crystals, from alcohol and toluene respectively, were found not to exhibit quite the same combination of forms; the crystals of the first crop showed all the forms enumerated with the exception of *r*, while those of the second crop were characterised by a combination of forms *b*, *a*, *m*, *p*, *c*, and *r*, and, moreover, were generally twins, with *b* as twin and composition plane. Typical crystals are shown in Figs. 6 and 7. The crystals were measured on the two-circle goniometer, and the observed and calculated values for the angles ϕ and ρ are given in the following table:

Fig. 6.

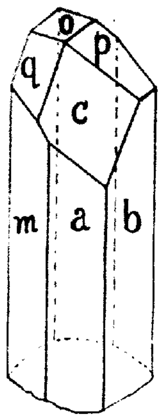
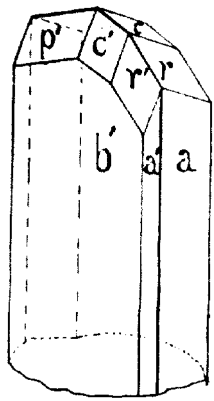


Fig. 7.



Phthalylphenylmethylhydrazide.
(Single crystal.) *Yellow modification (triclinic twin).*

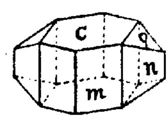
Form.	No.	Mean observed. φ.	Mean observed. ρ.	Calculated. φ.	Calculated. ρ.
b-{010}	8	0° 0′	90° 0′	—	—
a-{100}	8	*105 32	90 0	—	—
m-{110}	7	*130 56	90 0		—
p-{101}	4	*329 53	*27 31		—
c-{001}	3	60 53	*27 20	60°44′	—
r-{101}	1	87 1	49 5	87 19	49°21′
o-{111}	2	277 27	14 34	276 46	14 50
q-{01̄1}	2	109 54	25 45	110 22	25 41
a-(twin)	1	254 30	90 0	254 28	90 0
p-(twin)	1	210 15	27 38	210 7	27 31
c-(twin)	1	119 8	27 17	119 15	27 20
r-(twin)	1	92 36	49 0	92 41	49 21

Cleavage: perfect parallel to *b*-{010}, imperfect parallel to *m*-{110}. D_4^{21} 1·352. Molecular volume = 186·5.

(2) *Pale Modification.*

A typical crystal is shown in Fig. 8. The crystals are monoclinic with $a:b:c = 0{\cdot}7659 : 1 : 0{\cdot}5306$; $\beta = 92°10'$. Forms: *c*-{001}, *m*-{110}, *n*-{120}, *q*-{011}, and *o*-{111}; the last form was only observed once. The measured and calculated angles from three crystals are given in the following table:

Fig. 8.



Phthalylphenylmethylhydrazide (pale modification).

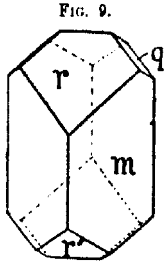
		Mean measured.		Calculated.	
Face.	No.	ϕ.	ρ.	ϕ.	ρ.
n·120	11	33°15′	—	33° 9′	—
m·110	11	*52 34	—	—	—
c·001	3	91 21	*2°10′	90 0	—
q·011	6	4 9	*28 1	4 17	—
o·111	1	54 9	42°15′	54 3	42°5′

Cleavage: parallel to basal plane {001} perfect. Optics: extinction on m 21°. An optic axis obliquely visible through {001}, and its position points to the optic axial plane being the plane of symmetry. Birefringence strong. D_4^{16} 1·327. Molecular volume = 189·9.

Phthalylphenylbenzylhydrazide, $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>N\cdot NPh\cdot CH_2Ph$.

Phthalylphenylbenzylhydrazide was prepared as before described from phthalic anhydride and phenyl benzylhydrazine. It crystallises from alcohol or toluene in bright orange-coloured, monoclinic prisms (compare Fig. 9) which melt at 132°. The pale-coloured modification has not yet been obtained:

FIG. 9.



Phthalylphenylbenzylhydrazide.

0·2656 gave 20·2 c.c. N_2 (moist) at 18° and 756 mm. N = 8·69.

$C_{21}H_{16}O_2N_2$ requires N = 8·54 per cent.

The calculated ratios of the axes are: $a:b:c = 0·8873:1:0·7729$; $\beta = 93°49'$, the observed forms being: $m-\{110\}$, $r-\{101\}$, $r'-\{\bar{1}01\}$, and $q-\{011\}$. The predominant terminal face was always $r-\{101\}$; the form $q-\{011\}$ was not present on all the crystals, and was very small.

		Limits.	Limits.	Mean.		Calculated.	
Face.	No.	ϕ.	ρ.	ϕ.	ρ.	ϕ.	ρ.
m·110	9	48°25′—48°34′	—	*48°29′	90° 0′	[illegible]	
r·101	3	89 36′—90 17	43° 6′—43°23′	89 54	*43 13	90° 0′	[illegible]
r'·$\bar{1}$01	3	89 46 —90 0	38 46 —38 59	89 53	*38 53	90° 0	—
q·011	2	4 31 — 4 43	37 43 —38 1	4 37	37 52	4 52	[illegible]

There was no observable cleavage; the optical extinction on the prism is 4° with the prism edge, on $r-\{101\}$ diagonal. D [illegible] Molecular volume = 264·5. The double refraction is strong.

Phthalyl-α-naphthylhydrazide, $C_6H_4<\substack{CO \\ CO}>N\cdot NH\cdot C_{10}H_7$.

Phthalyl-α-naphthylhydrazide, which was prepared in the ordinary manner from α-naphthylhydrazine, crystallises from alcohol in slender, orange-coloured, flattened prisms, which melt at 221°:

0·3944 gave 31·7 c.c. N_2 (moist) at 10° and 760 mm. N = 9·58.

$C_{18}H_{12}O_2N_2$ requires N = 9·7 per cent.

Phthalyl-β-naphthylhydrazide.

Phthalyl-β-naphthylhydrazide, prepared as before from β-naphthylhydrazine, crystallises from alcohol in slender, orange-coloured, flattened prisms, which melt at 184°:

0·2673 gave 21·7 c.c. N_2 (moist) at 10° and 760 mm. N = 9·67.

$C_{18}H_{12}O_2N_2$ requires N = 9·7 per cent.

Both phthalyl-α-naphthylhydrazide and phthalyl-β-naphthylhydrazide crystallise well from hot alcohol or toluene, in which they are sparingly soluble, but neither compound gave crystals adapted for measurement. Only the orange-coloured modification of each was obtained.

The authors desire to thank Mr. T. V. Barker for his kindness in measuring and examining all the crystals described, and for much help during the progress of the work, and also the Government Grant Committee of the Royal Society for a grant which has partly covered the cost of the material used.

UNIVERSITY CHEMICAL LABORATORY,
OXFORD.

CCLI.—*The Influence of Inactive Electrolytes on the Optical Activity of* l-*Malic Acid in Aqueous Solution.*

By CLIFFORD MORGAN STUBBS (1851 Exhibition Scholar of the University of New Zealand).

ALTHOUGH the influence of solvents on the rotatory power of optically active solutes has been much studied in recent years, much more work remains to be done before its nature will be made generally clear. A field not yet very widely explored is the case of the addition of electrolytes to aqueous solutions of active

substances. A study of the effect of this change of solvent on the rotation might be fruitful in helping to a solution of the general problem. Apart from cases where chemical reaction between solute and added electrolyte takes place (for example, in the formation of well known active hydroxy-acid complexes), the influence of inorganic salts has been investigated in the case of certain active sugars by several workers, for example, Farnsteiner (*Ber.*, 1890, **23**, 3570), Rimbach (*Zeitsch. physikal. Chem.*, 1892, **9**, 707), Rimbach and Weber (*ibid.*, 1905, **51**, 473), and Wender (*Biochem. Zeitsch.*, 1911, **30**, 357). The effects generally are small, increase with increasing salt addition, and in some cases show regularities according to the periodic system. In the present research it was attempted to make a systematic and exhaustive study of the influence of electrolytes on the rotation of *l*-malic acid. The great sensitiveness of the latter to various solution changes, for example its formation of abnormally active complexes with salts of certain multivalent elements, and the actual change from lævo- to dextro-rotation during concentration of its aqueous solution (Schneider, *Annalen*, 1881, **207**, 257), together with the large number of data which this sensitiveness has called forth, make malic acid eminently suitable for the investigation.

There is one very obvious objection to its use, however, which must here be met, namely, the fact that it is itself an electrolyte although a weak one, and that adjustment of ionic equilibrium will therefore complicate the observed effects. That this complicating influence is, however, very small is shown by the following calculation. In a typical case, to be described later, 0·25 of an equivalent of potassium chloride was added to 500 grams of a 20 per cent solution of malic acid. The system would come to equilibrium according to the equation:

$$\begin{array}{ccccccc} H\bar{A} & + & KCl & \rightleftharpoons & K\bar{A} & + & HCl \\ \alpha_1 & & \alpha_2 & & \alpha_3 & & \alpha_4 \\ 1-x & & n-x & & x & & x \end{array}$$

($\bar{A}$ represents the group $H_5C_4O_5$. The middle row gives the degree of dissociation, and the bottom row the gram-molecules present per V litres, of the various substances, when equilibrium is reached.) Then by a calculation due to Arrhenius and van Laar (compare also *Zeitsch. physikal. Chem.*, 1896, **19**, 485) the following equations are obtained:

$$\alpha_1\{(1-x)\alpha_1+(n-x)\alpha_2+x\alpha_3+x\alpha_4\}=kV(1-\alpha_1) \quad . \quad . \quad \text{(i)}$$

(k being the dissociation constant of $H\bar{A}$),

and $$(1-x)(n-x)\alpha_1\alpha_2=x^2\alpha_3\alpha_4 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

also, to a first approximation, $x^2=\dfrac{kV}{\alpha_3\alpha_4}$ . . . . (iii)

In the case under consideration, a_2, a_3, a_4 may be taken approximately equal, say, each to 0·78, the degree of dissociation of potassium chloride at the dilution used. It may be calculated that $V = 0·637$, and $n = 0·335$; also $k = 3·95 \times 10^{-4}$ (Ostwald, *Zeitsch. physikal. Chem.*, 1889, **3**, 369); hence from (iii), to a first approximation, $x = 0·0203$.

Therefore from (i), $a_1 = 0·00092$, and therefore from (ii) to a second approximation, $x = 0·01912$. Hence the percentage of potassium as hydrogen malate $= \frac{0·01912 \times 100}{0·335} = 5·706$; or percentage as undissociated hydrogen malate $= 5·706 \times 0·22 = 1·255$. The extent of ionic reaction is therefore in this and similar cases very small; and in actual practice any possible effect on the rotation due to it was completely overshadowed by large influences of another sort.

Experimental.

Apparatus and Method.—The rotation of the solutions was read by a Schmidt and Haensch three-field polarimeter; ten to fifteen readings being taken for each solution, in most cases an accuracy to within a few thousandths of a degree being attained. The temperature was in all cases 20°, the thermometer being standardised, and reading to tenths. Yellow sodium light was used, obtained from a flame illuminated by sodium chloride, and filtered through 2·5 cm. of a 6 per cent. solution of potassium dichromate, this giving (Landolt, "Das opt. Drehungsvermögen," p. 364) a mean wavelength of $589\mu\mu$. Density was determined by means of a pyknometer of about 15 c.c. content.

Kahlbaum's malic acid was used. Of the salts, most were the "pure, for analysis" salts used in the laboratory; a few had to be specially prepared; some (for example, zinc chloride) were obtained in solution, the strength of the latter being determined by analysis. For comparative purposes it was considered best to add the various salts in equivalent quantities to malic acid solutions of the same strength, namely, 100 grams of malic acid : 400 grams of water, in most cases. Such a solution is about 1·5 molecular, and, without being too concentrated, made possible sufficiently large and accurate results. Where the anhydrous electrolytes could not conveniently be used, hydrates or solutions of them were added to more concentrated malic acid solutions in such proportions that the ratio, malic acid : total water : equivalents of electrolyte, was as given. To make up the 20 per cent. solution above described, malic acid, dried over sulphuric acid until no further loss of weight occurred, was added to four times its weight of water. The composition determined by titration against barium hydroxide standardised by

succinic acid agreed satisfactorily with that by direct weighing. For five different 20 per cent. solutions prepared in the manner described from different samples of malic acid, the densities were:

d_4^{20} = (*a*) 1·0793, (*b*) 1·0797, (*c*), (*d*), and (*e*) 1·0795.

The mean density was thus 1·0795. Other densities determined were:

for 5 per cent. solution d_4^{20} = 1·0180
" 40 " " d_4^{20} = 1·1713.

On exhibiting these data graphically, the points lie on a regular curve passing through the point for which percentage = 0, and density = 1. If strengths and densities, as given by Schneider (*loc. cit.*), Nasini and Gennari (*Zeitsch. physikal. Chem.*, 1896, **19** 117), Woringer (*ibid.*, 1901, **36**, 336), and Winther (*ibid.*, 1902, **41**, 161), are similarly represented by curves, it is seen that considerable divergencies exist between the several results, the author's curve being the middle one of the five. Concentration calculated from a given density would be about 5 per cent. lower according to Schneider and Woringer than according to the author or Nasini and Gennari. Recognising these differences, Woringer ascribed them to error on Nasini and Gennari's part. Both the latter and he determined concentration by titration against potassium hydroxide. The author believes that his gravimetric preparation of the solutions yields consistent (compare constancy of density of independently prepared 20 per cent. solutions, shown above) and trustworthy results, whilst according to Degener (*Festsch. d. Techn. Hochschule, Braunschweig*, 1897, p. 451) doubt attaches to the accuracy of a titration of malic acid against alkali. If the author be right, and Woringer in error, the latter's data will evidently need revision; and the same holds regarding Thomsen's results (*Ber.*, 1882, **15**, 441), where the composition of malic acid solutions is determined from density by a formula based on Schneider's data.

Rotation of Pure Malic Acid Solutions (l = 2 dcm.).

TABLE I.

p.	α_D^{20}.	d_4^{20}.	$[\alpha]_D^{20}$.
5	− 0·229°	1·018	− 2·25°
20 (*a*)	− 0·38	1·0793	− 0·88
20 (*b*)	− 0·42	1·0797	− 0·97
20 (*c*)	− 0·415	1·0795	− 0·96
20 (*d*)	− 0·41	1·0795	− 0·95
20 (*e*)	− 0·469	1·0795	− 1·09
40	+ 0·500	1·1713	+ 0·535

The five different 20 per cent. solutions, for which data are tabulated above, were prepared from different samples of Kahl

baum's malic acid. A repetition of the measurements in the cases (*a*) and (*c*), where the rotation varies most from the mean, confirmed the values given. The constancy of the density in the five cases shows that there was no appreciable difference in the percentage composition of the solutions; hence it must be concluded that the figures in the last column indicate actual differences in the rotatory power of the malic acid used. The explanation is no doubt to be found in the difficulty of obtaining chemically pure a substance so liable to the influence of traces of impurities, to polymerisation, anhydride-formation, and possibly racemisation.

In the following tables n = number of equivalents of salt added to 500 grams of a 20 per cent. solution of malic acid. Under the

Effect of Alkali Salts on the Rotation.

TABLE II.

Salt.	n.	d^{20}_{4}.	a^{20}_{D}.	$[a]^{20}_{D}$.	$[a]^{20}_{D}$ for pure acid.	Δ.
CsCl	$\frac{1}{4}$	1·1442	0·363°	0·86°	−1·08°	1·94°
CsCl..........	1	1·3185	1·418	3·58	−1·08	4·66
RbCl	$\frac{1}{4}$	1·1223	0·369	0·87	−1·08	1·95
RbCl	1	1·2417	1·598	4·00	−1·08	5·08
KCl	$\frac{1}{8}$	1·0905	0·07	0·16	−0·88	1·04
KCl	$\frac{1}{4}$	1·1013	0·455	1·07	−0·88	1·95
KCl	$\frac{1}{2}$	1·123	1·09	2·61	−0·88	3·49
KCl	1	1·1618	1·895	4·69	−0·88	5·57
KNO_3	$\frac{1}{4}$	1·1095	0·388	0·92	−0·96	1·88
KNO_3	1	1·1882	1·404	3·55	−0·96	4·51
KBr	$\frac{1}{4}$	1·1215	0·49	1·16	−0·95	2·11
KBr	1	1·2363	2·015	5·05	−0·95	6·00
(*a*) KI	$\frac{1}{4}$	1·1397	0·608	1·44	−0·95	2·39
KI	1	1·3015	2·283	5·84	−0·95	6·79
(*b*) K_2SO_4	$\frac{1}{4}$	1·1126	0·222	0·52	−0·96	1·48
NaCl	$\frac{1}{4}$	1·0993	0·30	0·70	−0·97	1·67
NaCl	1	1·153	1·86	4·51	−0·88	5·39
$NaNO_3$	$\frac{1}{4}$	1·107	0·275	0·65	−0·96	1·61
$NaNO_3$	1	1·180	1·482	3·68	−0·96	4·64
Na_2SO_4	$\frac{1}{4}$	1·1103	0·082	0·19	−0·95	1·14
Na_2SO_4	$\frac{3}{4}$	1·181	1·021	2·43	−0·95	3·38
NH_4Cl.........	$\frac{1}{4}$	1·086	0·08	0·19	−0·97	1·16
NH_4Cl.........	1	1·103	0·92	2·31	−0·97	3·28
NH_4NO_3......	$\frac{1}{4}$	1·0938	0·064	0·15	−0·96	1·11
NH_4NO_3......	1	1·131	0·794	2·04	−0·96	3·00
$(NH_4)_2SO_4$ ...	$\frac{1}{4}$	1·0965	−0·126	−0·30	−0·95	0·65
$(NH_4)_2SO_4$ ...	1	1·1418	0·416	1·03	−0·95	1·98
LiCl...........	$\frac{1}{4}$	1·091	−0·105	−0·24	−0·97	0·73
LiCl...........	1	1·123	0·775	1·87	−0·97	2·84

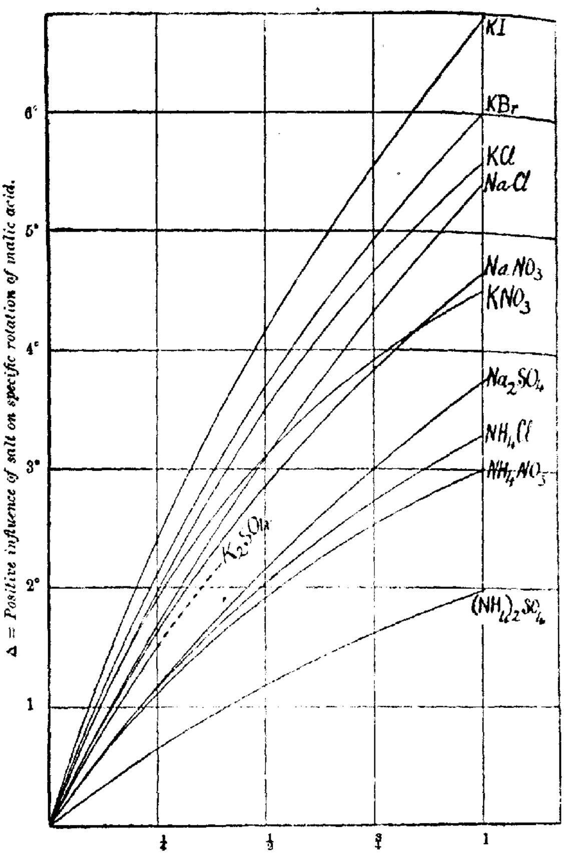
(*a*) Oxidation of the potassium iodide took place in the acid solution, which gradually turned brown; but when the readings were taken this action had probably not advanced far enough to affect them materially.

A projected measurement of the effect of potassium fluoride had to be abandoned, as sufficient hydrogen fluoride was liberated in the acid solution to have attacked and spoiled the glass polarimeter tube.

(*b*) Insufficient solubility prevented the use of a higher concentration of potassium sulphate.

column headed "$[\alpha]_D^{20}$ for pure acid" is given the specific rotation of the particular 20 per cent. solution of malic acid to which the salt was added. Δ denotes the change in a dextro-direction of the

FIG. 1.



n = number of equivalents of salt per 100 grams of anhydrous malic acid.

rotation caused by the addition of the salt, and is thus a measure of its influence on the rotation.

It is seen from the above table that in all cases the addition of the salts has markedly influenced the rotation, turning it in a

dextro-direction, and in most cases actually changing a lævo- into a dextro-rotation. If the typical case of potassium chloride is considered, it is seen how this influence, measured by Δ, varies continuously with the amount of salt added, Δ increasing as the amount of salt increases, but not quite proportionally. Fig. 1 shows graphically the influence of most of the alkali salts, Δ being plotted as ordinate, and the content in salt, n, as abscissa. There is thus obtained, for example, for potassium chloride, a very regular curve, passing through the origin and the four points determined, and with slight curvature convex upwards. For the other salts the data give only two points on each curve, besides the origin; but their position leaves no doubt that they lie on curves similar in point of regularity and of general appearance to that of potassium chloride. It was thought unnecessary to determine more points on these curves, those given illustrating with sufficient accuracy the nature of the result obtained.

The relative influences of the various salts are somewhat different at different concentrations; this is shown clearly in Fig. 1 by the varying curvature, and even crossing, of the curves. In investigating the connexion between the chemical nature of the salts and their comparative effects on the rotation, a definite equivalent concentration at which to compare these must therefore be chosen. An infinitely small concentration commends itself for this, for disturbing factors such as varying degree of dissociation of the salt, internal pressure, etc., will then be least evident; whilst at higher concentrations they may produce the divergencies from proportionality shown in the curves. Practical measurements of Δ being, however, impossible with a very small concentration of salt, an approximation will be obtained in comparing the values of Δ at the relatively low concentration for which $n = \frac{1}{4}$. Carrying out this comparison, it is evident from the curves that the influence of the salts on the rotation varies regularly with their chemical nature. For positive radicles the effects are in the order:

$$^{*}Cs > Rb > K > Na > NH_4 > Li;$$

for negative, $I > Br > Cl > NO_3 > \frac{1}{2}SO_4$. A numerical comparison reveals a striking regularity, shown by the following table:

TABLE III.

	Δ.	Diff.		Δ.	Diff.		Δ.	Diff.
KCl	1·95		KNO_3	1·88		$\frac{1}{2}K_2SO_4$ ...	1·48	
NaCl	1·67	0·28	$NaNO_3$ ...	1·61	0·27	$\frac{1}{2}Na_2SO_4$ ...	1·14	0·34
NH_4Cl......	1·16	0·51	NH_4NO_3...	1·11	0·50	$\frac{1}{2}(NH_4)_2SO_4$	0·65	0·49

* For "$n = \frac{1}{4}$" additions of salt the effects of cæsium, rubidium, and potassium chlorides are actually equal, but the shape of the curves (Fig. 2) seems to show that at lower concentrations of salt the order of influence is as given.

From the close agreement between the columns headed "Diff." it must be concluded that the effect of each of these alkali salts may be regarded as the sum of two terms, distinctive of the positive and negative radicles of the salt. The absolute value of the influence due to each radicle obviously cannot be decided, only the relative, for example, from the above table:

$$K - Na = \text{about } 0{\cdot}30^\circ.$$
$$Na - NH_4 = \text{about } 0{\cdot}50^\circ.$$
and consequently, $$K - NH_4 = \text{about } 0{\cdot}80^\circ.$$

From a consideration of the above results and those to be described, it seems probable that the main influence is exerted by the positive radicle.

Effect of Barium and Calcium Salts.

TABLE IV.

Salt.	n.	d_4^{20}.	a_D^{20}.	$[a]_D^{20}$.	$[a]_D^{20}$ for pure acid	Δ.
$BaCl_2$	¼	1·1256	1·976°	4·62°	−0·96°	5·58°
$BaCl_2$	1	1·2566	6·769	16·27	−0·96	17·23
(*a*) $Ba(NO_3)_2$	¼	1·133	1·652	3·88	−0·95	4·83
$CaCl_2$	¼	1·1018	1·226	2·86	−1·09	3·95
(*b*) $CaCl_2$	1·019	1·166	5·758	13·72	−1·09	[illegible]
(*b*) $Ca(NO_3)_2$	0·2998	1·1155	1·455	3·42	−0·95	[illegible]
$Ca(NO_3)_2$	1	1·1917	4·552	11·12	−0·95	[illegible]

(*a*) Insufficient solubility prevented the use of a higher concentration of barium nitrate.

(*b*) In these cases a too great quantity of salt was inadvertently added, as is shown under column "n." In the case of calcium nitrate, where the effect for $n = \frac{1}{4}$ is of interest for comparative purposes, interpolation gives 3·69° as the value of Δ for that concentration of salt.

The order of influence of the radicles of the above table is $Ba > Ca$, and as in the case of the alkali salts, $Cl > NO_3$. For the concentration $n = \frac{1}{4}$ we have:

TABLE V.

	Δ.	Diff.		Δ.	Diff.
$BaCl_2$	5·58°	1·63°	$Ba(NO_3)_2$ ...	4·83°	1·14°
$CaCl_2$	3·95		$Ca(NO_3)_2$ ...	3·69	

The numbers under "Diff." do not agree so closely as in the case of the alkali salts, barium nitrate giving a smaller effect than would be expected. It is very significant that, as appears from conductivity tables (Landolt-Börnstein, "Tabellen," p. 745), the dissociation of barium nitrate in aqueous solution at the concentration used is abnormally low; for whilst barium and calcium chlorides show practically equal degrees of dissociation in $N/2$-solution, that of barium nitrate is only about five-sixths that of calcium nitrate. A

connexion thus appears to exist between the degree of dissociation of a salt and its influence on the rotation of malic acid.

The most remarkable fact shown by table IV is the great influence exerted by salts of barium and calcium, especially when it is remembered that in equal equivalent concentrations there is only half an atom of these elements present to one atom of the alkalis. In order to determine whether this influence was connected with the valency of the metallic radicle, as well as to further the investigation generally, the effect of salts of other bivalent metals, and of the tervalent metal, aluminium, was measured.

Effect of Salts of Weaker Bases.

TABLE VI.

Salt.	n.	d_4^{20}.	a_D^{20}.	$[a]_D^{20}$.	$[a]_D^{20}$ for pure acid.	Δ.
$HgCl_2$	½	1·126	−0·257°	−0·60°	−0·96°	0·36°
$Hg(NO_3)_2$	½	1·1495	−1·893	−4·45	−1·09	−3·36
$Hg(NO_3)_2$	1	1·3472	−1·900	−4·67	−1·09	−3·58
$Cd(NO_3)_2$	½	1·1291	−0·150	−0·35	−1·08	0·73
$Cd(NO_3)_2$	1	1·267	0·831	2·03	−1·08	3·11
$ZnCl_2$	½	1·1105	−0·226	−0·53	−1·09	0·56
$ZnCl_2$	1·015	1·1915	0·613	1·46	−1·09	2·55
$Zn(NO_3)_2$	½	1·119	−0·229	−0·54	−1·09	0·55
$Zn(NO_3)_2$	1	1·2283	0·711	1·72	−1·09	2·81
$ZnSO_4$	½	1·118	−0·406	−0·95	−0·95	0·00
$ZnSO_4$	0·998	1·2247	0·045	0·11	−0·95	1·06
$MgCl_2$	½	1·0995	−0·137	−0·32	−1·09	0·77
$MgCl_2$	1	1·1556	0·729	1·73	−1·09	2·82
$Mg(NO_3)_2$	½	1·107	−0·061	−0·14	−0·95	0·81
$Mg(NO_3)_2$	1	1·1817	0·699	1·70	−0·95	2·65
$MgSO_4$	½	1·1095	−0·262	−0·61	−0·95	0·34
$MgSO_4$	1	1·1935	0·240	0·56	−0·95	1·51
$AlCl_3$	½	1·0985	−0·209	−0·49	−1·09	0·60
$AlCl_3$	1	1·1547	0·655	1·54	−1·09	2·63
$Al_2(SO_4)_3$	½	1·1075	−0·295	−0·69	−1·09	0·40

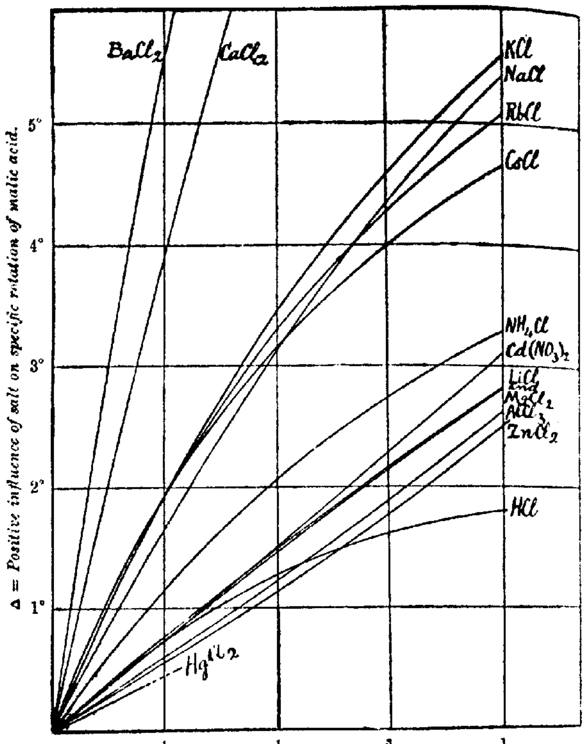
The curves in Fig. 2 show the respective effects of all the various chlorides used; also of cadmium nitrate, cadmium chloride not being used.

The effects of the salts mentioned in the above table is in general positive, and of the same order as that of the alkali and alkaline earth salts, although less in magnitude. It follows that the large influence of barium and calcium salts is not merely dependent on the valency of the metal. As was found in previous cases, so in table VI it is seen that the chloride and nitrate of any particular metal (with a notable exception, to which reference will be made later, in the case of mercury) exert about the same influence on the rotation, and the sulphate considerably less than either. The general effect of the metal radicles is in the order

$$Cd > Mg > Al > Zn > Hg.$$

More complicated relationships have, however, replaced the simple ones met with in the case of the alkali salts; so that to draw with any accuracy the curves representing the effects, more points than two or three would usually need to be determined. In every case previously studied, the effect when $n=1$ is less than four times

FIG. 2.



n = *number of equivalents of salt per* 100 *grams of anhydrous malic acid.*

that when $n=\frac{1}{4}$, and the corresponding curve is convex upwards. This still holds for magnesium chloride and magnesium nitrate but for the other salts in table VI, and notably those of zinc and mercury, the reverse is true. A striking illustration is the case of zinc sulphate, where the effect when $n=\frac{1}{4}$ is actually zero, that when $n=1$ being more than a degree. It thus appears that the

first addition of zinc sulphate produces a negative effect, making the rotation more lævo; and that as further quantities are added, the influence attains a negative maximum, passes again through zero, and becomes positive. The case of mercuric nitrate, if comparable, is more remarkable still. The figures (for $n = \frac{1}{4}$, $\Delta = -3 \cdot 36°$, and for $n = 1$, $\Delta = -3 \cdot 58°$) suggest that the initial large negative influence reaches a maximum between the two concentrations studied, and that further additions of salt would probably influence the rotation in a dextro-sense.

The cause of the greater complexity of the influence of these salts is doubtless connected with their being salts of much weaker bases than those previously studied, the complexity of the influence increasing with the weakness of the base. The incipient formation of feebly dissociated salts or complexes of malic acid appears a probable explanation. Malic acid is noted for its tendency to form with weakly basic metals complexes of a widely different rotation from the acid itself. On the addition to the acid of a salt of a weak base, a limited amount of the feebly dissociated malate or complex would be formed, and equilibrium set up according to the equation:

Salt of weak base and strong acid + malic acid $\rightleftarrows$
Feebly dissociated malate or complex + strong acid.

Thus, as actually observed, the initial addition of salt would affect the rotation in an anomalous manner, depressing its value if the malate or complex formed were strongly lævorotatory; whilst further additions would affect it more normally. To test this explanation, a rough experiment was performed in the case of the "$n = 1$" solution of zinc nitrate and malic acid (table VI), nitric acid being added in successive small equal quantities to the solution, and its effect on the rotation observed. If the above explanation be correct, the first additions of nitric acid should diminish the amount of the feebly dissociated malate or complex, according to the equation, and thus influence the rotation more powerfully in a dextro-direction than subsequent additions, the effect of which would be only the ordinary one of acids on malic acid (see table VIII). That this actually occurred, the following table shows:

TABLE VII.

No. of parts of nitric acid added.	Observed angle of rotation.
0	0·71°
3	0·98
7	1·19
13	1·33
23	1·54

Effect of Acids.

TABLE VIII.

Acid.	n.	d_4^{20}.	α_D^{20}.	$[\alpha]_D^{20}$.	$[\alpha]_D^{20}$ for pure acid.	Δ
HCl	½	1·0875	−0·105°	−0·25°	−0·97°	[illegible]
HCl	0·859	1·105	0·315	0·75	−0·97	[illegible]
HNO_3	½	1·089	−0·195	−0·46	−0·96	[illegible]
HNO_3	1	1·1153	0·255	0·64	−0·96	[illegible]
H_2SO_4	½	1·0947	−0·229	−0·54	−1·09	[illegible]
H_2SO_4	1	1·1385	0·294	0·71	−1·09	[illegible]
$C_2H_4O_2$	½	1·0812	−0·432	−1·03	−1·09	[illegible]
$C_2H_4O_2$	1	1·0855	−0·304	−0·78	−1·09	[illegible]

Schneider (*Annalen*, 1881, **207**, 278) investigated the effect of sulphuric and acetic acids on a considerably weaker solution of malic acid than that employed in the present research, and found that both changed the rotation in a dextro-sense, the former, however, tenfold more so than the latter. The measurements tabulated above for these acids are in harmony with his result. Acetic acid exerts a regular and positive, but notably small, influence, a fact to which future reference will be made.

Some small part of the influence of the acids must be due to their throwing back the small electrolytic dissociation of the malic acid, but it is as hydrogen salts that they have their chief effect. The latter is, for the mineral acids, regular and somewhat smaller than that of the alkali salts. Hydrochloric acid exerts a less influence than lithium chloride, so that in order of influence K>Na>Li>H, parallel to the order of atomic weights. Nitric acid has less influence than hydrochloric acid, as was to be expected; but sulphuric acid breaks the usual order, $Cl>NO_3>\frac{1}{2}SO_4$, in that it lies between hydrochloric and nitric acids in its effect. The explanation of this exception is not clear; it may possibly be due to the fact that HSO_4 ions are largely present instead of the SO_4 ions in other sulphate solutions.

Effect of Salts on Solutions of Varying Concentration.

Hitherto the influence of electrolytes has been considered on the specific rotation of 20 per cent. solutions of malic acid only. It was thought of interest to determine how that influence varied, both absolutely and relatively, with respect to different salts when the concentration of the acid was varied. For this purpose the effect of potassium chloride and of sodium chloride was studied on 5 per cent. and 40 per cent., as well as on 20 per cent. solutions of malic acid. In table IX, p=percentage of malic acid solution; n= number of equivalents of salt added per 100 grams of pure malic acid; other symbols have their usual meaning.

TABLE IX.

Salt.	p.	n.	d_4^{20}.	a_D^{20}.	$[a]_D^{20}$.	$[a]_D^{20}$ for pure acid. (a.)	Δ.
KCl	5	¼	1·0235	−0·161°	−1·59°	−2·25°	0·66°
KCl	5	1	1·0405	−0·034	−0·34	−2·25	1·91
KCl	5	4	1·1043	0·335	3·50	−2·25	5·75
NaCl	5	¼	1·023	−0·183	−1·81	−2·25	0·44
KCl	20	¼	1·1013	0·455	1·07	−0·88	1·95
NaCl	20	¼	1·0993	0·30	0·70	−0·97	1·67
KCl	40	¼	1·2132	3·573	3·96	0·535	3·425
NaCl	40	¼	1·2083	3·417	3·74	0·535	3·205

(a) For this column see table I.

(b) These figures are taken from table II.

The relative effect of equivalent quantities of potassium chloride and sodium chloride is seen to be about the same for each strength of acid solution, in each case potassium chloride exercising somewhat more influence than sodium chloride. A similar result may be inferred to hold for the influence of salts generally.

The values of Δ given for the three different concentrations of potassium chloride in the case of 5 per cent. acid solutions show the regularity of the influence exerted, even when (as for $n=4$) the molar concentration of the salt considerably exceeds that of the acid. If these values are considered along with the other results obtained for potassium chloride (tables II and IX) a simple and important relation is seen to obtain between Δ and the potassium chloride concentration of the solutions examined. Let N denote the number of equivalents of potassium chloride per 100 c.c. of solution (p and Δ same as before); then, with the necessary calculations, the following is obtained:

TABLE X.

p.	N.	Δ.
5	0·0128	0·66°
5	0·052	1·91
5	0·221	5·75
20	0·0273	1·04
20	0·055	1·95
20	0·112	3·49
20	0·232	5·57
40	0·121	3·425

It is evident that Δ depends mainly on N, and but little on p; in other words, the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of malic acid present. Each malic acid molecule may be regarded as affected independently of other malic acid molecules, but to a degree dependent on the

number of salt molecules or ions within its sphere of influence. What little departure the above table shows from this rule is explicable by the varying malic acid present causing a variation in properties of solvent and salt, for example, by affecting the degree of dissociation. It may be mentioned that Farnsteiner's work on the influence of salts on the rotation of sucrose reveals a quite analogous law (*Ber.*, 1890, **23**, 3750).

Effect of Salts of Weak Acids.

It has been calculated above (p. 2266) that the action of malic acid on salts of strong bases and strong acids is negligible. This would not, however, hold in the case of a salt of a weak acid. It was thought of interest to determine the effect in one or two cases of an acetate, which is the salt of an acid weaker even than malic.

TABLE XI.

Salt.	n.	d^{20}_{4}.	a^{20}_{D}.	$[a]^{20}_{D}$.	$[a]^{20}_{D}$ for pure acid.	Δ
$KC_2H_3O_2$	$\frac{1}{4}$	1·1000	−0·762°	−1·82°	−0·95°	[illegible]
$KC_2H_3O_2$	1	1·1540	−2·216	−5·74	−0·95	[illegible]
$Ba(C_2H_3O_2)_2$	$\frac{1}{4}$	1·1235	1·26	2·98	−0·97	[illegible]
$Ba(OH)_2$	0·2435	1·1195	1·069	2·49	−0·97	[illegible]

For "$n=\frac{1}{4}$" concentration, potassium acetate gave an effect of −0·87°, as against +1·95° for potassium chloride. This negative effect (in contrast with the case of mercuric nitrate) was more than quadrupled on quadrupling the amount of salt added. The contrast between the influence of potassium acetate and that of other potassium salts is explained by the large formation in the former case of hydrogen malate and undissociated acetic acid. The extent and effect of this action may be approximately calculated for the "$n=\frac{1}{4}$" addition of potassium acetate. In the following scheme the symbols mean the same as in the somewhat similar calculation on p. 2266.

$$\begin{array}{cccccc} H\bar{A} & + & KC_2H_3O_2 & \rightleftharpoons & K\bar{A} + & H\cdot C_2H_3O_2 \\ a_1 & & a_2 & & a_3 & a_4 \\ 1-x & & n-x & & x & x \end{array}$$

Let k_1 and k_2 be the respective dissociation constants of malic and acetic acids, and C the concentration of hydrion in solution. The following well-known relations will hold:

$$C \times \{a_1(1-x) + a_3x\} = k_1 \times (1-a_1)(1-x) \quad . \quad . \quad . \quad \text{(i)}$$

and $$C \times \{a_2(n-x) + a_4x\} = k_2 \times (1-a_4)x \quad . \quad . \quad . \quad . \quad \text{(ii)}$$

∴ by division, $$\frac{a_1(1-x) + a_3x}{a_2(n-x) + a_4x} = \frac{k_1(1-a_1)(1-x)}{k_2(1-a_4)x} \quad . \quad . \quad . \quad \text{(iii)}$$

Now a_3 may be taken approximately equal to a_3; and a_1, and particularly a_4, are very small. Also, $k_1 = 3{\cdot}95 \times 10^{-4}$, $k_2 = 1{\cdot}8 \times 10^{-5}$. Hence, equation (iii) reduces approximately to:

$$x^2 = \frac{395}{18}(1-x)(n-x).$$

Now, as in the former calculation, $n = 0{\cdot}335$.

$\therefore x = 0{\cdot}3263$; that is, $\frac{0{\cdot}3263}{0{\cdot}335}$ or 97·4 per cent. of the potassium acetate has been acted on and hydrogen malate formed.

An estimate may now be made of the order of the rotation the solution might be expected to show. The rotation should mainly consist of (*a*) the rotation of the potassium hydrogen malate, (*b*) that of the excess of untransformed malic acid, and (*c*) the influence of the potassium hydrogen malate and acetate, similar to that of other salts, on the rotation of the excess of malic acid. For (*a*), interpolation from the data of Schneider (*Annalen*, 1881, **207**, 266), with necessary calculation, gives $-0{\cdot}99°$ as the actual rotation of 200 mm. of a solution of potassium hydrogen malate of the same concentration as has been calculated to be present above. For (*b*), similar interpolation and calculation from the author's data in table I give $-0{\cdot}41°$ as the rotation caused by the residual unchanged malic acid (amounting to 67·4 per cent. of the whole). For (*c*), assuming the influence to be approximately equal to that of an equivalent quantity of potassium chloride, calculation gives 0·55°. Adding these three effects, the observed rotation α of the solution should thus be about $-0{\cdot}99° - 0{\cdot}41° + 0{\cdot}55° = -0{\cdot}85°$. The angle actually observed was $-0{\cdot}76°$. The agreement between the results of calculation and observation is at least sufficiently good to show that the abnormal negative influence of potassium acetate, and even its order of magnitude, might have been anticipated.

Barium salts (table IV) exert so large an influence on the rotation of malic acid that the question suggests itself whether here, at least, the formation of a chemical complex or undissociated salt is accountable. Considering the strongly basic nature of barium, such a thing is a priori improbable; yet the large influence referred to, considered in conjunction with the extraordinarily sharp ascent to a large dextrorotation determined by Schneider for barium malate, even in dilute solution (*loc. cit.*, p. 277), makes it desirable to answer the question with greater certainty. The results for the addition of barium acetate and barium hydroxide, tabulated above, enable this to be done. If a complex or feebly dissociated malate were formed, a much greater effect would be expected in these cases than when the hydrochloric acid is competing for the barium. Tables IV and XI show, however, that, on the contrary, and as in

the case of potassium acetate, the acetate and hydroxide of barium cause considerably less dextrorotation than the chloride.

The table shows that barium hydroxide was added in somewhat smaller proportions than the barium acetate, in fact, so as to produce in solution the amount of barium hydrogen malate which a calculation similar to that made in the case of potassium acetate would show to be formed when the barium acetate was added. As would be expected if the apparent influence of the acetate were due to an almost complete formation of hydrogen malate, the effect of the barium hydroxide was only a little less than that of the barium acetate. The difference of 0·49° is to be explained by (i) the slightly greater amount of barium in the latter case influencing the rotation of the unchanged malic acid by 0·1° to 0·2°; (ii) the one-fourth equivalent of acetic acid present in the latter case exercising (see table VIII) a small effect on the rotation, say, 0·1°; (iii) the more dilute solution in the former case, due to the water of neutralisation; this would rather lower the observed rotation.

Effect of Electrolytes on Malates.

Thomsen (*J. pr. Chem.*, 1887, [ii], **35**, 145) found that excess of alkali had a considerable influence on the rotation of alkali salts of malic and other hydroxy-acids, which he ascribed to the formation of complexes, the excess of alkali combining with the alcoholic hydroxyl. The evidence offered in support does not seem strong, no such complex being prepared, and the main argument apparently being the observed effect on the rotation. It seemed worth investigating whether sodium chloride affected sodium malate similarly to excess of sodium hydroxide. The solutions were prepared of such strength that they may be considered to consist of 20 per cent. malic acid solution, together with the amount of anhydrous sodium hydroxide or chloride required for the equivalent proportions. In the following table, $[\alpha]_D^{20}$ is calculated as the specific rotation of the malic acid present; Δ is the positive increase in $[\alpha]$ due to addition of the extra sodium hydroxide or chloride molecule

TABLE XII.

Equivalent proportions.	d_4^{20}.	α_D^{20}.	$[\alpha]_D^{20}$.	Δ
$C_4H_6O_5 + 2NaOH$	1·171	−3·123°	−7·46°	
$C_4H_6O_5 + 3NaOH$	1·2226	−1·524	−3·67	3·79
$C_4H_6O_5 + 2NaOH + NaCl$	1·2172	−2·006	−4·97	2·49
*$C_4H_6O_5 + 2NaOH$	1·1716	—	−7·42	
*$C_4H_6O_5 + 3NaOH$	1·2222	—	−3·71	3·71

* The last two lines are obtained by interpolation and calculation from Thomsen's results; they agree well with the author's data, in the first two lines.

It appears that sodium chloride produces a dextro-effect on the rotation about two-thirds of that produced by sodium hydroxide; thus the influence is at least of the same order; and if, as seems likely, the influence of sodium chloride is not due to a complex, it cannot be said, apart from further evidence, that the influence of sodium hydroxide is so caused. Other substances than sodium hydroxide would presumably similarly influence the rotation of sodium malate. It is interesting to note that, if two molecules of sodium chloride had been first added to the 20 per cent. malic acid instead of two of sodium hydroxide, the third molecule of sodium chloride would, by extrapolation from the results in table II (if such extrapolation can be trusted), have an influence on the rotation of approximately the same magnitude, 2·5°; at any rate, not more.

Discussion of Results and Conclusions.

Inactive electrolytes might influence the rotation of a solution of malic acid in two ways: (i) by affecting the composition or constitution of the active molecules; (ii) by setting in operation solution-forces which would affect the asymmetry of the molecules. Change in composition might come about, in the first place, by the salts forming complexes with the malic acid, an explanation which, with a possible exception in the case of a few of the salts of table VI, may on the following grounds be dismissed as most improbable: (*a*) the regular nature of the salt influence; (*b*) the *a priori* inconceivability of a salt like potassium chloride forming such complexes; and (*c*) the evidence already given against complex formation in the case of barium chloride. Secondly, the malic acid might act on the salts, forming malates and liberating acids; but calculation, confirmed by experiment, has shown that this only occurs to an extent of any importance when the salt of a weak acid, such as acetic, is added; thus, in a solution of malic acid and potassium chloride, the partial formation of potassium hydrogen malate, which is lævorotatory (Schneider, *loc. cit.*, p. 266), could not explain the large dextro-influence observed. Thirdly, change of molecular composition might be due to change of electrolytic or other dissociation in the presence of the salts; but the magnitude of the effects observed is far too great to be explained by change of electrolytic dissociation, whilst it appears highly improbable that polymerisation would be largely influenced by the presence of the salts.

The cause of the salt-influence must, then, be sought elsewhere than in change of composition or constitution of the active substance. An explanation plausible at first sight is that the formation in solution of hydrated molecules by the added salts

would act like concentrating the solution, which is well known to influence the rotation of malic acid in a dextro-sense (Schneider, *loc. cit.*, p. 262). That such an action, if occurring at all, is relatively insignificant, is shown (i) by the fact that the magnitude of the salt-influence is often far too great to be thus explained, barium chloride, for example, producing at the higher concentration an effect several times as great as would be given by total dehydration of the malic acid (assuming Schneider's value of [illegible] for the rotation of the anhydrous acid); (ii) by the fact that, in general, the salts with greatest affinity for water, such as lithium chloride, actually exercise the least influence.

Light would be thrown on the salt-effects could a parallelism be discovered between them and any other physical properties of the solutions. The result of a search made by the author for such a parallelism may be summarised as entirely negative; this applies not only to purely physical properties, such as viscosity and density of the solutions, mass of salt added, etc., but also to the physico-chemical action of salts in precipitating colloids, and their influence on the solubility of non-electrolytes in water (Rothmund, "Löslichkeit und Löslichkeitsbeeinflussung," p. 148). It is specially noteworthy that the internal pressure of aqueous solutions of the various salts (see Tammann, "Beziehungen zwischen den inneren Kräften und Eigenschaften der Lösungen," p. 87) shows no significant parallelism to the effects of the salts on the rotation of malic acid. This fact bears on Patterson's attempt (Trans., 1901 and following years) to establish a general connexion between the "solvent influence" on rotation and the internal pressure of the solutions.

The above failure to connect the observed effects of electrolytes on the rotation of malic acid with ordinary chemical or physical changes confirms the view that the influence is mainly due to a direct and distinctive power possessed by the inactive molecules in solution to affect the asymmetry of the active ones within their sphere of influence without actual chemical combination. The law deduced on p. 2277 that "the influence of the salt on the specific rotation depends mainly on the concentration of the solution with regard to that salt, and not on the concentration of malic acid," thus receives its explanation. Further, (i) from the additive nature of the effect of strong positive and negative radicles (p. [illegible]); (ii) from the smallness of the effect of mercuric chloride and acetic acid, the two practically non-ionised substances used; (iii) from the parallelism between unexpectedly low influence and low conductivity in the case of barium nitrate; and (iv) from the consideration that most of the properties of solutions of electrolytes are actually

mic, it is reasonable to conclude that the large effects tabulated this paper are chiefly produced by the ions.

The nature of this ionic influence can be little more than rmised. For positive univalent ions the influence is in the order the electro-affinities in aqueous solution, thus:

$$Cs > Rb > K > Na > Li > H,$$

hilst for negative univalent ions the reverse is the case, thus: Br > Cl > NO_3. Passing to bivalent ions, this parallelism is oken. ½Ba and ½Ca have an influence greatly exceeding that the more positive Cs; and ½SO_4 less than that of the more gative NO_3. The unexpected place that sulphuric acid was seen occupy in the order of influence of acids may be due to the nivalent HSO_4 ions affecting the rotation much more than SO_4 is. With the exception, however, of cadmium, which is between ic and mercury in its electro-affinity, the bivalent metal ions show mong themselves a similar parallelism, thus:

$$Ba > Ca\ (> Cd) > Mg > Zn > Hg.$$

is connexion between electro-affinity and ion-influence is striking. As for the mode of the influence, it appears plausible that it may connected with the sensitiveness of the alcoholic hydroxyl of lic and other hydroxy-acids, which is liable to be attacked with formation of complexes showing unusually large rotation. The s within the sphere of influence of a malic acid molecule may the centres of forces which, acting on the sensitive hydroxyl oup, change the asymmetry or rotatory power of the molecule. this is the point of influence, malic anions ought to be similarly sitive to ionic influence—an expectation confirmed by facts (see 2281). It is worthy of note that when the hydroxyl group had n attacked and a chemical complex formed, Rosenheim and g (*Ber.*, 1899, **32**, 3432) found that the great sensitiveness of lic acid to changes of concentration disappeared.

f the above view is correct, light is thrown on the general nature he often otherwise inexplicable influence of solvents on rotation. thout any change of molecular composition or constitution (as ally understood), the interaction of the "residual affinities" of molecules of solute and solvent may affect the degree of asym- ry of the former, just as malic acid molecules are influenced by ghbouring ions in aqueous solution.

sidelight of great interest on the above data and discussion has to be mentioned. Schneider (*Annalen*, 1881, **207**, 257) sured the specific rotation, $[\alpha]_D^{20}$, in aqueous solutions of various centration of malic acid, the malates and hydrogen malates of ssium, sodium, lithium and ammonium, and barium malate.

He found the specific rotation of malates to vary with the concentration, even more than that of malic acid. Moreover, the diversity of rotation shown by the various malates (see his diagram, *loc. cit.*, facing p. 368) is not merely due to his plotting specific rotations against percentage compositions of the solution, for when calculations are made from his data, and molecular rotations plotted against molar concentrations, the diversity persists in a no less striking form. This might be expected at higher concentrations of dissolved salt, where the influence of the metallic radicles in the undissociated molecules is naturally felt. The interesting fact is that at lower concentrations the differences in molecular rotations of the various salts persist in such a way that only the barest approximation holds to Oudemans' law, namely, that salts of an active acid and inactive base show the same molecular rotation in very dilute solutions. Schneider's data for barium malate do not allow of extrapolation of any accuracy; the following table shows the values given by him (*loc. cit.*, p. 284), by extrapolation from an empirical formula, for the molecular rotations at infinite dilution of the alkali malates.* The last column shows the corresponding values obtained by the author from graphical extrapolation.

TABLE XIII.

Malate of	$[M]_D^{20}$ at inf. dilution (Schneider).	$[M]_D^{20}$ at inf. dilution (graphically).
KH	$-10.65°$	$-10.4°$
NaH	-10.95	-11.0
LiH	-11.87	-12.5
K_2	-15.35	-15.5
Na_2	-17.52	-16.2
Li_2	-18.56	-19.2

The above table shows beyond doubt that, according to Schneider's results, Oudemans' law is only approximately obeyed. In the case of both malates and hydrogen malates, the molecular rotation at infinite dilution of the potassium salt is more dextro- than that of the sodium salt, and the latter than that of the lithium salt, an order of effect remarkably parallel to that given for the salts in table II, namely K>Na>Li. On the view which the author has taken, the explanation is simple. The metallic ions of the dissociated malates retain the power to influence the asymmetry of the malic anion, just as the ions of salts have been seen to affect malic acid molecules and anions (tables II and XII). At infinite dilution this influence persists, for, unlike the case in which the ions of electrolytes influence malic acid molecules by their chance proximity

* Owing to hydrolysis probably commencing at low concentrations, the figures for the malate of the weak ammonium are not very significant.

the positively charged cations must by electrostatic forces be kept always within the sphere of influence of the negatively charged active anions. Hence if alkali cations influence the rotation of malic or hydromalic anions in the same order (K>Na>Li) as they influence the undissociated molecules, just such deviation from Oudemans' law would be expected as actually observed. It may be added that the rapidly increasing dextrorotation of barium malate is probably due (in part, at least) to the influence on the malic anions of the barions, which have been seen (table IV) to have an extraordinarily great influence on malic acid itself.

If the above view of the invalidity of Oudemans' law in this case is correct, it is evident that colorimetric and other discrepancies cited against the ionic hypothesis may really be an indication of a similar continued mutual influence of the dissociated ions.

The influence of the alkali salts on the rotation of malic acid shows a regularity hitherto unmentioned. In general, the rate of the initial influence of a salt is not sustained, but falls off as its concentration increases. The regularity referred to consists in the fact that the rate of influence of the alkali chlorides, for example, falls off more rapidly the higher the atomic weight of the metal. This is shown in Fig. 2 by the increasing curvature of the curves from lithium chloride to cæsium chloride. No explanation of this behaviour has been found.

In conclusion, it may be said that a systematic confirmation and extension of some of the older work on malic acid and malates seems called for, using purer materials, more accurate instruments, etc. The determination, in very dilute solutions, of the rotation of malates, their electrolytic dissociation, and the effect of various salts on their rotation, would be a valuable contribution to the subject.

Finally, the author is of the belief that electrolytes will exercise a similar influence on tartaric and other hydroxy-acids—a matter perhaps worthy of investigation.

Summary.

(1) Certain other workers (especially Schneider and Woringer) appear to have erred in the determination of the strength of their malic acid solutions, and their data need revision accordingly.

(2) Electrolytes in general exercise a large influence on the rotation of malic acid solutions, turning it in a dextro-direction.

(3) This influence is mainly a specific additive property of the radicles or ions; it is notably great in the case of alkaline earth salts; and it appears to be related with the valency of ions and their order of electro-affinities.

(4) The influence of electrolytes is shown not to be in general due to complex-formation or ionic reaction, or to hydrate-formation by the electrolytes.

(5) The asymmetry of the malic acid molecules is affected by the ions within their sphere of influence, to an extent dependent on the concentration of electrolyte, and not largely on that of malic acid. No connexion has been found with other properties of electrolyte solutions.

(6) Thomsen's supposed complex-formation between sodium malate and excess of alkali appears explicable on the ground of similar ionic influence on the malic anions.

(7) The divergencies of the alkaline malates (according to Schneider's data) from obeying Oudemans' law appear explicable on the ground of the continued influence of the dissociated but necessarily adjacent ion; (the same may hold for other apparent contradictions of the ionic hypothesis).

The author desires to express his indebtedness to Professor F. G. Donnan, whose suggestions and advice were invaluable throughout the course of the work.

THE MUSPRATT LABORATORY OF PHYSICAL AND ELECTROCHEMISTRY,
UNIVERSITY OF LIVERPOOL.

CCLII.—*Organic Derivatives of Antimony. Part II. The Orienting Influence of Antimonic Substituents in the Benzene Nucleus.*

By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

PHOSPHORUS, arsenic, and antimony differ markedly from nitrogen, the initial member of this periodic family of elements, in regard to the degree of hydration exhibited by their oxy-acids, and this difference persists in the organic derivatives of these acids. Nitric acid, which yields metallic salts derived from the meta-hydrate $HO{\cdot}NO_2$, gives rise to organic nitro-compounds corresponding exclusively with its least hydrated form. On the contrary, the organic derivatives of phosphorus, arsenic, and antimony, like the metallic salts of the oxy-acids of these elements, exhibit types corresponding with the more hydrated pyro- and ortho-acids, as well as compounds derived from the meta-acids.

Accordingly these three elements can each furnish three series

of compounds derived from their ortho-oxy-acids, as illustrated in the following scheme, where X is phosphorus, arsenic, or antimony, and R a univalent alkyl or aryl group:

$HO{\cdot}XO(OH)_2$	$(HO)_2XO{\cdot}OH$	$(HO)_3X{:}O$
	$\downarrow$	$\downarrow$
$R{\cdot}XO(OH)_2$	$R_2XO{\cdot}OH$	$R_3X{:}O$

Some of the compounds of the third series are found to exist in the hydrated form, $R_3X(OH)_2$, which corresponds with the true ortho-hydrate, $X(OH)_5$.

When substitution occurs in nitrobenzene the introduction of the entrant substituent follows the meta-law of substitution. Nitration and sulphonation, for example, lead mainly to the production of *m*-dinitrobenzene and nitrobenzene-*m*-sulphonic acid. In this respect the nitro-group is analogous to the carboxyl and sulphonic groups, which are similarly derived from meta-acids:

meta-Acids.	Phenyl compound.	1:3-Di-derivative.
$HO{\cdot}NO_2$	$C_6H_5{\cdot}NO_2$	$C_6H_4(NO_2)_2$
$HO{\cdot}CO_2H$	$C_6H_5{\cdot}CO_2H$	$C_6H_4(NO_2){\cdot}CO_2H$
$HO{\cdot}SO_3H$	$C_6H_5{\cdot}SO_3H$	$C_6H_4(NO_2){\cdot}SO_3H$

This being the behaviour of meta-acidic groups in reactions involving substitution, it becomes of interest to ascertain what law of substitution is followed in the presence of such acid groups as $XO(OH)_2$, $:XO{\cdot}OH$, and $:X{:}O$ or $:X(OH)_2$.

Although a very large amount of work has been carried out, chiefly by Michaelis and his pupils, on aromatic compounds containing phosphoric, arsenic, and antimonic substituents, yet the influence of these groups on the orientation of entrant radicles has not been studied systematically; for example, in the phosphorus series it is surmised that, in nitrophenylphosphinic acid, the nitro-group enters a meta-position with respect to the phosphoric radicle (Michaelis and Benzinger, *Annalen*, 1877, **188**, 273), but in the case of trinitrotriphenylphosphine oxide the nitro-groups are assumed to take up para-positions (Michaelis and Soden, *Annalen*, 1885, **229**, 326). Some uncertainty still exists in regard to the arsenic series, although recent researches on atoxyl and allied compounds have shown that the nitration product of phenylarsinic acid is the meta-compound (Michaelis and Lösner, *Ber.*, 1894, **27**, 263; Bertheim, *ibid.*, 1908, **41**, 1655; 1911, **44**, 3297).

The organic antimony derivatives have recently acquired importance owing to the belief that some of these substances might prove to be of therapeutic interest. The present communication deals mainly with the nitration of the three series of antimony compounds and with the orientation of the products.

(1) *Monophenyl Series.*—**An interesting point has arisen in connexion with the preparation of phenylstibine dichloride, the starting point in this series. The dichloride was first prepared by Hasenbäumer (*Ber.*, 1898, 31, 2910) by heating triphenylstibine and antimony trichloride in xylene at 240°. In a recent communication Michaelis and Günther (*Ber.*, 1911, 44, 2316) state that the reaction leads to the formation of diphenylstibine chloride, which they isolated in comparatively poor yield. We find that both these observations are correct, our experiments showing that the condensation is a balanced reaction in the sense indicated by the following equations:**

$$2(C_6H_5)_3Sb + SbCl_3 = 3(C_6H_5)_2SbCl,$$
$$(C_6H_5)_2SbCl + SbCl_3 \rightleftharpoons 2C_6H_5\cdot SbCl_2.$$

Phenylstibine dichloride, which according to our experience is the main product of the foregoing change, yields phenylstibinic acid on successive chlorination and hydrolysis. The nitration product of this acid consists chiefly of m-*nitrophenylstibinic acid*, for on heating at 110—120° with phosphorus pentabromide (3 mols.) the antimonic group is eliminated, and 1-bromo-3-nitrobenzene is produced:

$$NO_2\cdot C_6H_4\cdot SbO(OH)_2 + 3PBr_5 = NO_2\cdot C_6H_4\cdot SbBr_4 + 3POBr_3 + 2HBr$$
$$NO_2\cdot C_6H_4\cdot SbBr_4 = NO_2\cdot C_6H_4Br + SbBr_3.$$

This result might have been predicted by applying the Crum Brown and Gibson rule. The hydrogen derivative of the antimonic substituent is $H\cdot SbO(OH)_2$, assuming this to be a possible form of antimonious acid. Now since this acid is directly oxidisable to antimonic acid, the corresponding radicle, $\cdot SbO(OH)_2$, like the NO_2 and CO_2H groups, should induce substitution in the meta-position. The groups $\vdots SbO\cdot OH$ and $\vdots SbO$ or $\vdots Sb(OH)_2$ are present in the diphenyl and triphenyl series, and since the corresponding hydrogen compounds are unknown, it is impossible to predict what would be their behaviour towards oxidising agents. Accordingly the rule cannot be applied to these cases.

(2) *Diphenyl Series.*—The nitration product of diphenylstibinic acid is rather more stable than *m*-nitrophenylstibinic acid and the trinitro-derivative of triphenylstibinic acid, but on heating at 150—160° with phosphorus pentabromide (2 mols.) and bromine (1 mol.) it undergoes fission into antimony bromide and 1-bromo-3-nitrobenzene:

$$(NO_2\cdot C_6H_4)_2SbO\cdot OH + 2PBr_5 = (NO_2\cdot C_6H_4)_2SbBr_3 + 2POBr_3 + HBr.$$
$$(NO_2\cdot C_6H_4)_2SbBr_3 + Br_2 = 2NO_2\cdot C_6H_4Br + SbBr_3.$$

The group $:SbO \cdot OH$ accordingly induces substitution of a NO_2 radicle in the meta-position.

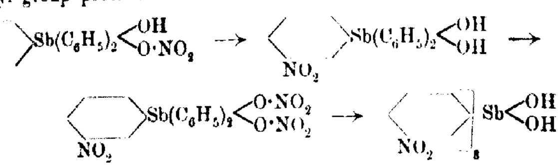
(3) *Triphenyl Series*.—Triphenylstibinic acid (triphenylstibine dihydroxide) furnishes a trinitro-derivative, which is proved to be chiefly the meta-compound by fission at 110° with phosphorus pentabromide (2 mols.) and bromine (2 mols.):

$$(NO_2 \cdot C_6H_4)_3Sb(OH)_2 + 2PBr_5 = (NO_2 \cdot C_6H_4)_3SbBr_2 + 2POBr_3 + 2HBr.$$

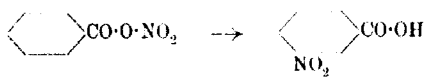
$$(NO_2 \cdot C_6H_4)_3SbBr_2 + 2Br_2 = 3NO_2 \cdot C_6H_4Br + SbBr_3.$$

The 1-bromo-3-nitrobenzene collected was about 70—80 per cent. of the calculated quantity.

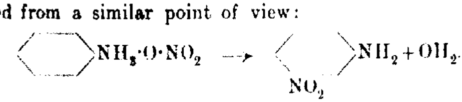
In the triphenyl series it is of interest to note that intermediate nitration products can be isolated when less concentrated nitric acid is employed. Triphenylstibine nitrate and hydroxynitrate have both been described, and it is therefore probable that the first stage of nitration in these three series of stibinic acids is the formation of nitrates, the nitro-group becoming first attached to an oxygen of the antimonic substituent, and subsequently migrating into the ring in the meta-position, this process being repeated until each phenyl group present is nitrated:



Cases in which the migrating group passes from the side-chain to a meta-position in the ring are very uncommon, but an interesting comparison may be drawn between the foregoing nitrations and the transformation of benzoyl nitrate into *m*-nitrobenzoic acid:



(Francis, *Ber.*, 1906, **39**, 3798). The production of *m*-nitroaniline from aniline nitrate and concentrated sulphuric acid may be regarded from a similar point of view:



EXPERIMENTAL.

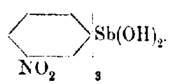
Triphenylstibine, the starting point of this investigation, was first prepared by Michaelis and Reese in the interaction of antimony

trichloride, chlorobenzene, and sodium in dry benzene (*Annalen*, 1886, **233**, 39), and since produced by Pfeiffer through the Grignard reaction (*Ber.*, 1904, **36**, 4620), the yield being about 60 per cent. of the weight of trichloride employed.

The following modified process gave an almost quantitative yield of this substance. A 10 per cent. benzene solution containing 18 grams of antimony trichloride was slowly added to the Grignard reagent prepared from 50 grams of bromobenzene and 7·2 grams of powdered magnesium suspended in dry ether, and the mixture boiled for six hours and then distilled in steam. The fusible organic residue was freed from diphenyl by extraction with small quantities of cold alcohol, and the undissolved triphenylstibine (m. p. 48°) was further purified by crystallisation from hot alcohol, although this treatment was not generally necessary.

A similar result was obtained by using antimony tribromide, but the sparing solubility of this halide in benzene necessitated the employment of more dilute solutions.

If in these condensations with antimony trichloride or tribromide the benzene solution is filtered from the precipitate of magnesium compounds and worked up without distillation in steam, the product consists in part of triphenylstibine dichloride or dibromide, but these compounds of quinquevalent antimony are converted into triphenylstibine by reduction with alcoholic ammonium sulphide as recommended by Kaufmann (*Ber.*, 1908, **41**, 2762).

Tri-m-nitrotriphenylstibinic Acid, 

The nitration experiments were carried out on triphenylstibine hydroxynitrate, a compound already described as resulting from the interaction of triphenylstibine dichloride and silver nitrate (Trans., 1910, **97**, 35). This crystalline hydroxynitrate can also be prepared by adding triphenylstibine to a 30 per cent. solution of fuming nitric acid in glacial acetic acid. Nitrous fumes are evolved, and after the violent reaction has subsided, the liquid is gently warmed and poured into water. The recrystallised hydroxynitrate melts at 220°.

Twenty-five c.c. of nitric acid (D 1·5) decolorised with carbamide were mixed with 6 c.c. of concentrated sulphuric acid and maintained at 40° while 3 grams of the hydroxynitrate were slowly added, the temperature being afterwards raised to 55°. After two hours the cooled solution was poured on ice, the precipitated nitro-compound dissolved in warm *N*-sodium hydroxide, and reprecipitated by hydrochloric acid.

Tri-m-nitrotriphenylstibinic acid is a pale orange-yellow powder, crystallisable from glacial acetic acid in light yellow leaflets. Its decomposition point is somewhat indefinite, ranging in different preparations from 170° to 191°. This variation is possibly due to the presence of varying amounts of para- and ortho-isomerides. The compound is, however, identical with the substance obtained by May on nitrating triphenylstibine (Trans., 1910, **97**, 1958), this being demonstrated by comparative experiments on the two methods of preparation.

The alkali salts of tri-*m*-nitrotriphenylstibinic acid are soluble in water to a brownish-orange solution, which on boiling acquires an odour of nitrobenzene. The barium, strontium, calcium, magnesium, copper, silver, cobalt, and lead salts obtained by double decomposition from the soluble alkali and ammonium salts are all sparingly soluble.

Orientation Experiments with Tri-m-nitrotriphenylstibinic Acid.

Preliminary trials with aqueous potassium hypobromite showed that the acid is oxidised destructively by this reagent. Heating with iodine chloride in glacial acetic acid solution effected the elimination of antimony, but the mixed iodo- and chloro-derivatives of nitrobenzene which were simultaneously produced could not be separated and identified.

(1) One gram of tri-*m*-nitrotriphenylstibinic acid was heated for twelve hours at 115—130° with 15 c.c. of chloroform saturated with hydrogen bromide. The contents of the tube were distilled in steam, but no nitrobenzene could be detected. This experiment, which was duplicated, showed that hydrogen bromide alone did not decompose the nitro-compound into antimony tribromide and nitrobenzene.

(2) A sealed tube containing 1 gram of nitro-acid, 2 grams of phosphorus pentabromide, and 1 gram of bromine in 15 c.c. of chloroform was heated at 130—160°, and although some charring occurred, the yield of 1-bromo-3-nitrobenzene was 70 per cent. of the calculated quantity.

(3) One gram of nitro-acid and 3 grams of bromine heated in chloroform at 115—130° gave on distilling in steam 0·7 gram of 1-bromo-3-nitrobenzene, and 0·25 gram of the unchanged nitro-compound was recovered; the eliminated antimony was precipitated and weighed as sulphide, the calculated amount being obtained.

(4) Experiment 2 was repeated, using dry sodium tri-*m*-nitrotriphenylstibinate instead of the free acid, and adding triethylamine to fix the hydrogen bromide produced during the decomposition. The contents of the tube were distilled in steam, when the only volatile product obtained was 1-bromo-3-nitrobenzene.

(5) **Two grams of tri-*m*-nitrotriphenylstibinic acid,** 5 grams of **bromine, and 15 c.c. of water were heated for several** days at 160°, **and then for twenty-seven hours at temperatures** ranging from 150° to 270°. The product when freed from excess of bromine and distilled in steam yielded 1·2 grams of 1-bromo-3-nitrobenzene, and the residue gave 0·3 gram of brominated product, probably 1 : 3 : 4-tribromo-5-nitrobenzene (m. p. 119°).

(6) The crude tri-*m*-nitrotriphenylstibinic acid when boiled with excess of *N*-sodium hydroxide furnished a small amount of nitrobenzene arising probably from the hydrolysis of the para- and ortho-isomerides of this acid, which are not present to the extent of more than 10 per cent.

Tri-m-*aminotriphenylstibine*, $Sb(C_6H_4 \cdot NH_2)_3$.

Two grams of tri-*m*-nitrotriphenylstibinic acid were slowly introduced into 100 c.c. of boiling alcohol containing 5 grams of zinc dust and 0·8 gram of ammonium chloride. The mixture was heated and shaken for half an hour, and then filtered into 100 c.c. of ice-cold water. The precipitated base was dissolved in dilute hydrochloric acid, and the *tri*-m-*aminotriphenylstibine* set free by ammonia:

0·1858 gave 0·3727 CO_2 and 0·0811 H_2O. C = 54·69; H = 4·85
0·1030 „ 0·2039 CO_2 „ 0·0455 H_2O. C = 54·00; H = 4·91
0·2542 „ 22·8 c.c. N_2 at 24·5° and 760 mm. N = 10·03.
0·2654 „ 0·1006 Sb_2O_4. Sb = 29·93.

$C_{18}H_{18}N_3Sb$ requires C = 54·54; H = 4·54; N = 10·6; Sb = 30·30 per cent.

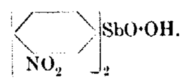
Tri-*m*-aminotriphenylstibine is obtained in colourless crystals from glacial acetic acid only with considerable difficulty; it decomposes indefinitely at about 80°. The base dissolves sparingly in alcohol or water, and is but slightly soluble in acetone, benzene, and other volatile organic media.

The crystalline *hydrochloride*, $Sb(C_6H_4 \cdot NH_2,HCl)_3$, is readily soluble in alcohol or water, but is precipitated from the latter by concentrated hydrochloric acid. Aqueous solutions of the salt are acid to litmus. The base and its salts, either in the solid state or in hot solutions, have a curious pungent odour, and cause violent fits of sneezing.

The hydrochloride was examined physiologically by Dr. Plimmer and by Mr. Hindle; it has a certain trypanocidal power, but nothing like so strong as lithium antimonyl tartrate, and its irritant effects are very acute, causing ulceration at the point of injection.

The base forms the following sparingly soluble salts: picrate, platinichloride, and diazonium chloride; the last of these condenses with alkaline β-naphthol to form an insoluble, red azo-compound. The base itself in neutral or acetic acid solution couples with diazobenzenesulphonic acid to produce a soluble azo-colouring matter.

Under the most favourable conditions the reduction of tri-*m*-nitrotriphenylstibinic acid does not proceed quite smoothly, being accompanied by elimination of antimony from combination with the organic groups. This destructive reduction becomes more pronounced when tin and hydrochloric acid are employed, and a considerable amount of aniline is produced. Tri-*m*-aminotriphenylstibine is not the sole product, as both reducing agents give rise to another basic substance which is soluble in alkali hydroxides as well as in acids; this product, which was not obtained crystalline and has no melting point below 230°, may possibly be tri-*m*-aminotriphenylstibine hydroxide.

Di-m-nitrodiphenylstibinic Acid, 

The process employed by Michaelis and Reese (*loc. cit.*) for the preparation of diphenylstibine trichloride was adopted with slight modifications. Antimony trichloride (48 grams) and chlorobenzene (48 grams) dissolved in 150—200 c.c. of dry benzene were added in the cold to 20 grams of sodium which had been previously granulated by melting and shaking under boiling toluene. When a vigorous reaction did not take place spontaneously, it was started by cautiously warming the mixture. After twenty-four hours the solution was filtered from precipitated antimony and unaltered sodium; the benzene and toluene were evaporated away, the oily residue triturated with alcoholic hydrochloric acid till it solidified, and then dissolved in the minimum amount of boiling alcohol. The major portion of the triphenylstibine dichloride (m. p. 141°) crystallised out on cooling, and the mother liquor was concentrated until a second crop of crystals separated. This fraction, which consisted of impure diphenylstibine trichloride, was purified by extraction with hot dilute hydrochloric acid. The acid solution filtered from undissolved triphenylstibine dichloride deposited on cooling lustrous, colourless, lath-like crystals of diphenylstibine trichloride (m. p. 176°). This preparation was repeated several times, and the yields of diphenylstibine trichloride varied from 11 to 16 per cent. of the weight of antimony trichloride employed.

For purposes of nitration the trichloride was dissolved in alcohol, and converted, by means of silver nitrate, into a basic nitrate,

crystallising in clusters of lustrous, colourless needles, and decomposing at 206° with evolution of nitrous fumes.

Four grams of this basic nitrate were added to 56 c.c. of nitric acid (D 1·5) mixed with 20 c.c. of concentrated sulphuric acid; the temperature was maintained at 40°, and afterwards raised to 55°. The clear, yellow solution was then cooled, and poured on to ice; the pale yellow product was dissolved in *N*-sodium hydroxide and reprecipitated by acetic or hydrochloric acid:

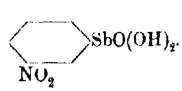
0·2925 gave 18·0 c.c. N_2 at 29° and 768 mm. N = 6·78.
0·3248 „ 0·1254 Sb_2O_4. Sb = 30·48.
$C_{12}H_9O_6N_2Sb$ requires N = 7·05; Sb = 30·22 per cent.

When crystallised from glacial acetic acid, *di*-m-*nitrodiphenylstibinic acid* separated in radiating clusters of flattened needles, which decomposed somewhat indefinitely at 212°. The nitrated product before dissolving in aqueous alkali decomposes at 220—230°, evolving nitrous fumes; it probably consists, at least in part, of a nitrate or basic nitrate.

Di-m-*nitrodiphenylstibinic acid* is insoluble in water, alcohol, or benzene; its alkali salts are soluble in water to an orange-yellow solution; the other metallic salts obtained by double decompositions are very sparingly soluble.

Orientation Experiments.—Preliminary trials showed that di-m-nitrodiphenylstibinic acid was more stable than tri-*m*-nitrotriphenylstibinic acid. Sealed tubes containing the dinitro-acid, phosphorus pentabromide (2 mols.), and bromine (1 mol.) were heated at 100°, 125°, and 130—160°. At the two lower temperatures no change occurred, but after heating for eight to nine hours at the higher temperature the organic antimony compound was decomposed, and on distilling in steam the product yielded 1-bromo-3-nitrobenzene (m. p. 56°). The residue consisted of antimony oxybromide and a small amount of viscid decomposition product.

The experiment at 130—160° was repeated with phosphorus pentabromide alone with a similar result; the volatile product was 1-bromo-3-nitrobenzene, and rather more tar was left in the residue.

m-*Nitrophenylstibinic Acid*, 

Phenylstibine dichloride, the starting point in the preparation of monophenylated antimony compounds, was first prepared by Hasenbäumer (*loc. cit.*), and considerable quantities of this material were obtained by his process, which, however, was found to give diphenylstibine chloride as a by-product (Michaelis and Günther, *loc. cit.*).

A series of sealed tubes each containing 5 grams of triphenylstibine, 6·5 grams of dry antimony trichloride, and 12 c.c. of xylene dried over sodium was heated for forty-eight hours at 240°; the liquid contents of the tubes were filtered from a black, insoluble impurity, shaken three times with dilute hydrochloric acid, dried over calcium chloride, and distilled up to 200° under the ordinary pressure. The oily residue was then fractionated under considerably diminished pressure (about 5—7 mm.), when about three-fourths of the material distilled between 160° and 200°, and the remainder was collected between 200° and 240°. Twenty-four grams of triphenylstibine yielded an equal weight of the lower, and about 6—7 grams of the higher, fraction; the latter, which consisted mainly of diphenylstibine chloride, soon solidified, and the crystals then melted at 60°, the melting point being raised to 6[illegible]° after draining. The more volatile fraction, which consisted mainly of phenylstibine dichloride mixed with a smaller proportion of diphenylstibine chloride, either remained viscid or deposited crystals of the main constituent, which after draining melted at 55—58°.

Each of the foregoing fractions was suspended in dry cooled ether and treated with chlorine. In both cases the solution deposited colourless crystals, but whereas the crystals from the lower fraction melted at the ordinary temperature to a viscid oil, those from the higher fraction remained solid, and after crystallisation from dilute hydrochloric acid melted at 176°, and were thus identified as diphenylstibine trichloride.

The oily chlorine additive compound, consisting of impure phenylstibine tetrachloride, was hydrolysed with aqueous ammonia, when a solid residue was produced and identified as diphenylstibinic acid by conversion into diphenylstibine trichloride (m. p. 176°) by dissolving in hot alcoholic hydrochloric acid. The ammoniacal solution, which contained the greater part of the product of hydrolysis, was acidified with hydrochloric acid, when phenylstibinic acid was precipitated.

The solid chlorine additive compound was also hydrolysed by prolonged digestion with aqueous ammonia, when the greater part of the material remained undissolved, and was identified as diphenylstibinic acid. The ammoniacal filtrate when neutralised yielded a small quantity of phenylstibinic acid.

The Behaviour of Diphenylstibinic Acid towards Aqueous Alkalis.—Inasmuch as phenylstibinic acid is soluble in ammonia or aqueous sodium carbonate as well as in sodium hydroxide solution, and diphenylstibinic acid is described as being soluble in aqueous sodium hydroxide, but not in ammonia or sodium carbonate

solutions, these differences might serve to effect the separation of the two acids in the mixtures obtained in the foregoing experiments. However, the behaviour of diphenylstibinic acid is not invariable in this respect, and its solubility in alkalis depends on the mode of formation.

Diphenylstibine trichloride was dissolved in alcohol and treated with dilute ammonia, when a granular precipitate was obtained insoluble in aqueous ammonia or sodium carbonate. Another portion of this trichloride was dissolved in aqueous sodium hydroxide, and the solution acidified with acetic acid; the diphenylstibinic acid thus precipitated is readily soluble in aqueous ammonia or sodium carbonate.

These two preparations are in all probability differently hydrated modifications of diphenylstibinic acid, the less soluble form being possibly the meta-compound, $Ph_2SbO{\cdot}OH$, whilst the more soluble product may be either the ortho- or pyro-compound.

Nitration of Phenylstibinic Acid.—Three grams of this acid were nitrated in 27 c.c. of pure nitric acid (D 1·5) and 9 c.c. of concentrated sulphuric acid, the temperature ranging from 40° to [illegible]. The cooled solution when poured on to ice gave a yellow precipitate, which probably consists in part of a nitrate or basic nitrate, since on heating it decomposes with the evolution of nitrous fumes. The product was dissolved in dilute aqueous sodium hydroxide, and m-*nitrophenylstibinic acid* precipitated as a pale yellow compound on acidifying with acetic or hydrochloric acid. The acid dissolves in glacial acetic acid, but does not crystallise at all readily; it has no melting point below 290°:

0·3232 gave 13·7 c.c. N_2 at 27° and 760 mm. N = 4·68.
0·3814 „ 0·1976 Sb_2O_4. Sb = 40·91.
$C_6H_6O_5NSb$ requires N = 4·79; Sb = 41·10 per cent.

Orientation Experiments.—One gram of *m*-nitrophenylstibinic acid, suspended in 15 c.c. of chloroform with 6 grams of phosphorus pentabromide, was heated at 100—110° for four hours, and the product then distilled in steam; 1-bromo-3-nitrobenzene was obtained, the yield being about 70 per cent. of the calculated amount. The residue contained a small quantity of tar.

Triphenylstibinedihydroxidetrisulphonic Acid.

The sulphonation of triphenylstibine dihydroxide proceeds less smoothly than that of the previously described triphenylstibine hydroxysulphate (Trans., 1910, **97**, 37), and accordingly the latter compound was generally employed for this purpose. Triphenylstibine dichloride sulphonates, evolving hydrogen chloride, but the

use of this dichloride offers no advantages. May's experiments (Trans., 1910, **97**, 1958) show that the sulphonation of triphenylstibine itself is not a practicable operation, since the base acts as a reducing agent towards concentrated sulphuric acid, and becomes converted into triphenylstibineoxide sulphate.

Eight grams of the hydroxysulphate mixed with 20 c.c. of concentrated sulphuric acid were treated with 20 c.c. of fuming sulphuric acid (25 per cent. SO_3), the mixture heated at 100° for two to three hours, after which another 20 c.c. of fuming acid were added. The solution was left for twelve hours, poured on to ice, and the liquid neutralised with barium carbonate. The filtrate, freed from barium by the cautious addition of dilute sulphuric acid, was concentrated until of oily consistence, when alcohol produced a white precipitate. The filtrate was further concentrated, and treated repeatedly with alcohol and ether until a white deposit was no longer obtained. The final filtrate on evaporation left a clear, yellow oil, which was washed repeatedly with ether and dried over phosphoric oxide in a vacuum desiccator. Finally, a brittle, yellow mass was obtained resembling amber, the yield being about 40 per cent. of the weight of hydroxysulphate:

0·1806 gave 0·2068 CO_2 and 0·0600 H_2O. C=31·23; H=3·69.
0·4392 „ 0·5128 CO_2 „ 0·1112 H_2O. C=31·84; H=2·81.
0·1864 „ 0·0478 Sb_2S_3. Sb=18·32.
$C_{18}H_{23}O_{14}S_3Sb$ requires C=31·80; H=3·3; Sb=17·67 per cent.

These numbers agree with the formula:

$$(HO)_2Sb(C_6H_4\cdot SO_3H)_3,3H_2O;$$

the values for sulphur (16·0) were less concordant (theory=14·14 per cent.), showing that the compound still contains a small amount of more highly sulphonated organic compounds, but owing to the very soluble hygroscopic nature of the acid further purification could not be effected.

When titrated with standard sodium hydroxide and phenolphthalein, the compound was found to have a molecular weight of 667, on the assumption that it is a tribasic acid, the molecular weight calculated from the above formula being 679.

The metallic salts of triphenylstibinedihydroxidetrisulphonic acid are soluble in water; the sodium salt when triturated successively with phosphorus pentachloride and water yields a hydroxy-chloride, $(C_6H_4\cdot SO_2Cl)_3SbCl\cdot OH$, which dissolves in benzene, and is precipitated therefrom by light petroleum as a granular powder, decomposing indefinitely at 110°:

0·1280 gave 0·1072 AgCl. Cl=20·72.
$C_{18}H_{13}O_7Cl_4Sb$ requires Cl=20·32 per cent.

The white substances precipitated by alcohol or by a mixture of this solvent and ether during the evaporation of solutions of the foregoing trisulphonic acid were found to be mixtures produced by the condensation of antimonic acid and benzenemono- and di-sulphonic acids, their formation being the sequel to the destructive action of concentrated sulphuric acid on the organic antimony compound.

One of these products was prepared synthetically by heating together an aqueous suspension of antimonic acid and benzenesulphonyl chloride. The latter compound underwent hydrolysis, the antimonic and benzenesulphonic acids condensed to yield a soluble compound, which was deposited as a white, microcrystalline precipitate on adding alcohol to the concentrated aqueous solution. This compound, which may be regarded as a complex anhydride of the two acids, is readily soluble in water to a faintly acid solution, and contains about 29 per cent. of antimony and 18 per cent. of sulphur.

Physiological experiments by Dr. Plimmer showed that even in fatal doses triphenylstibinedihydroxidetrisulphonic acid and the above-mentioned benzenesulphonylantimonic acid derivatives do not act as effective trypanocides.

We desire to express our thanks to Mr. G. S. Whitby, B.Sc., A.R.C.S., who collaborated in the earlier experiments, and to the Government Grant Committee of the Royal Society for a grant which has partly defrayed the expenses of this investigation.

ROYAL COLLEGE OF SCIENCE, LONDON,
SOUTH KENSINGTON, S.W.

CCLIII.—*The Preparation of the Ketones of the Higher Fatty Acids.*

By THOMAS HILL EASTERFIELD and CLARA MILLICENT TAYLOR (New Zealand Government Research Scholar).

THE distillation of barium and calcium salts, although of general application as a method for obtaining ketones, suffers from the drawbacks that large quantities of salt cannot be conveniently treated in one operation, and that the yield of ketone is often unsatisfactory. Krafft (*Ber.*, 1882, **15**, 1712) has shown that with fatty acids of high molecular weight the yield is improved by

heating the salts under diminished pressure, and Young (*Trans.*, 1891, **59**, 621) obtained no less than 80 per cent. of the theoretical yield of the ketone of phenylacetic acid by controlling the temperature at which the calcium salt was decomposed, and ensuring the rapid removal of the volatile products of the reaction. Kipping (*Trans.*, 1890, **57**, 532) obtained a 40 per cent. yield of stearone by heating stearic acid with phosphoric oxide. This very convenient method is, however, inapplicable to the higher unsaturated fatty acids. The observation (Easterfield and Bagley, *Trans.*, 1904, **85**, 1244) that in the presence of iron filings abietic acid is readily deprived of its carboxyl group with formation of a hydrocarbon suggested that iron filings might determine the formation of ketones from fatty acids at comparatively low temperatures. This is actually the case with the acids from lauric to melissic acid; thus stearic acid gave an 80 per cent. yield of stearone when heated with powdered cast-iron turnings to 360—370° for a period of three hours.

The hitherto undescribed ketones of the higher fatty acids can be prepared by the same process, but owing to decomposition the yield is not so good.

There can be little doubt that a ferrous salt is first formed, and that this then undergoes decomposition. Ferrous stearate heated to 360° slowly decomposes, and yields about 60 per cent. of stearone.

No satisfactory yield of ketone was obtained by the interaction of iron turnings and acetic, butyric, phenylacetic, benzoic, suberic, and sebacic acids, or with the acid ester of sebacic acid.

The observation that ketones may result by the interaction of acids and metals was first made by Liebig and Pelouze, who obtained acetone by passing the vapour of acetic acid through a heated iron tube, but obtained negative results when a porcelain tube was employed. Jahn (*Ber.*, 1880, **13**, 2107) obtained acetone and impure butyrone respectively by passing the vapours of the corresponding acids over heated zinc dust. Hébert (*Compt. rend.*, 1903, **136**, 682) obtained a mixture of stearone with solid and liquid hydrocarbons by distilling stearic acid with magnesium powder at as low a temperature as possible. Finally, Mailhe (*Bull. Soc. chim.*, 1909, [iv], **5**, 616) found that ketones are the chief products of the interaction of the vapours of the lower fatty acids, from acetic to nonoic acid, with many reduced metals, including such feebly electropositive metals as lead and copper, which in the form of ordinary filings are almost without action on the fatty acids.

The formation of stearone by the action of iron on stearic acid probably accounts for the fact recorded by P. W. Robertson (*Trans. N. Z. Inst.*, 1904, 576) that the last runnings in the commercial

distillation of stearin are so rich in stearone that the melting points of successive portions of the distillate fall rapidly to a eutectic and then rise with even greater rapidity. Examination of the higher distillates obtained in the refining of "distillation ..." shows that they similarly contain oleone.

Experimental.

Preparation of Stearone.—Pure stearic acid was heated with ... tenth of its weight of sifted, clean cast-iron turnings to ..., at which temperature the evolution of carbon dioxide became perceptible. The temperature was then raised slowly to 36..., and maintained between 360° and 370° for two hours. After removal of the iron and free acid, the ketone was twice crystallised from ... petroleum (b. p. 100—120°), with the addition of animal charcoal, and it then melted at 88°. (Found, C = 82·71; H = 14·01. Calc., C = 83·00; H = 13·83 per cent.) The yield of crude stearone melting at 85° was 80 per cent. of that demanded by theory.

In dealing with large quantities of stearic acid it is advisable to raise the temperature rapidly to about 300°, and then to be very cautious about the further rise of temperature, as a sudden frothing sometimes commences at 320—330°.

The following table shows the comparative yields of stearone in a series of experiments made with the object of ascertaining the most suitable conditions of reaction. Column 1 gives the quantity of iron employed, expressed in terms of that theoretically required for the conversion of the whole of the acid into ferrous stearate. Columns 2, 3, and 4 give the percentage of the theoretical yield of ketone formed at the temperature indicated.

Percentage of iron.	Yield at 330°.	Yield at 360°.	Yield at 365°.
100	53	62	80
66	35	53	74
33	3	34	—
20	—	28	—

Unaltered iron remained in the experiments in column 4, an increase in the relative quantity of iron beyond the theoretical quantity did not improve the yield of ketone.

The experiments were carried out as follows: Test-tubes containing 1 gram of stearic acid and the requisite quantity of powdered cast-iron turnings were heated in a Lothar Meyer air-bath for three hours, the last 50° rise of temperature being allowed to occupy one hour, at the end of which time the evolution of carbon dioxide had practically ceased. The product was treated with acid and alkali, and then once crystallised from alcohol, weighed, and th...

melting point taken. In no case did the melting point differ by more than 4° from that required for the pure ketone. Very little ketone is formed if stearic acid or calcium stearate is heated to 360° or if stearic acid is heated with metallic iron at temperatures below 300°.

A sample of ferrous stearate prepared by adding ferrous acetate solution to an alcoholic solution of sodium acetate gave on analysis: Fe = 8·9. Calc., Fe = 9·0 per cent. This was heated to 360° for three hours, and the mass extracted with boiling alcohol; a 60 per cent. yield of stearone was obtained. Manganese stearate under similar conditions yielded 42 per cent. of ketone.

Good yields, up to 65 per cent., have been obtained by substituting aluminium and manganese for iron in the above operation.

Diheptadecylcarbinol, $(C_{17}H_{35})_2CH\cdot OH$.

The attempt to reduce stearone by means of ethyl alcohol and a very large excess of metallic sodium was unsuccessful, practically the whole of the ketone being recovered unchanged. Even with sodium and boiling amyl alcohol the reduction takes place but slowly.

One gram of stearone was dissolved in 200 c.c. of boiling amyl alcohol, and 8 grams of sodium were added in small portions at a time during a period of eight hours. The carbinol which crystallised out on cooling was recrystallised from amyl alcohol, and melted at 89·5°. It is much more soluble in ethyl alcohol than the ketone from which it is prepared.

The *acetate* prepared from the carbinol melted at 54—61°. Lack of sharpness in the melting point was observed by Kipping (Trans., 1890, **57**, 987) in the case of dipentadecylcarbinyl acetate prepared from palmitone, and the same phenomenon is noticed in the acetates of the carbinols obtained from cerotone and montanone:

0·1240 gave 0·3674 CO_2 and 0·1517 H_2O. C = 80·80; H = 13·54.

$C_{37}H_{74}O_2$ requires C = 80·73; H = 13·45 per cent.

Cerotone, $C_{51}H_{102}O$.

According to Beilstein (Vol. I., p. 1006), cerotone was obtained by Brückner by the distillation of lead cerotate, and melted at ?°, but the ketone prepared by Nafzger on distillation of the free acid melted at 92°. Mr. T. Rigg, M.Sc., kindly undertook the investigation of the action of iron turnings on cerotic acid, and supplies the following note.

The cerotic acid was prepared from beeswax by combining the methods of Brodie and of Marie, and melted at 77·5° (uncorr.).

Nine grams of the acid were heated with 0·69 gram of sifted cast-iron turnings, the temperature being allowed to rise to 350°, at which temperature the mixture was maintained for four hours. Evolution of carbon dioxide began at about 280°. After removal of iron and unchanged cerotic acid, the product of the reaction was recrystallised from light petroleum (b. p. 80—100°) until the melting point was constant. The yield was 55 per cent.; in a second experiment, in which the temperature was maintained at 360° for three hours, a 70 per cent. yield was obtained.

Cerotone prepared in this way melts at 93°; it is moderately soluble in light petroleum or ethyl acetate. It separates from hot glacial acetic acid in feathery groups of crystals. In hot ethyl alcohol it is almost insoluble, the solution merely becoming slightly turbid on cooling. (Found, C=83·50; H=13·93. Calc., C=83·5[illegible]; H=13·97 per cent.)

Dipentecosylcarbinol, $(C_{25}H_{51})_2CH{\cdot}OH$, prepared by reducing cerotone with sodium in boiling amyl-alcoholic solution, melted at 95°. The *acetate* prepared from this alcohol melted at 58—60°:

0·1068 gave 0·3207 CO_2 and 0·1315 H_2O. C=81·89; H=13·67.
$C_{53}H_{106}O_2$ requires C=82·17; H=13·69 per cent.

Cerotoneoxime, $(C_{25}H_{51})_2C{:}NOH$, was prepared by boiling 1 gram of cerotone dissolved in 150 c.c. of amyl alcohol with 2 grams of hydroxylamine hydrochloride and excess of potassium hydroxide. It was crystallised from ethyl acetate, and melted at 78°:

0·1227 gave 0·3696 CO_2 and 0·1505 H_2O. C=82·15; H=13·61.
0·44 „ NH_3 equivalent to 4·95 c.c. *N*/10-HCl. N=1·58.
$C_{51}H_{103}ON$ requires C=82·14; H=13·82; N=1·87 per cent.

Montanone, $(C_{27}H_{55})_2CO$.

Montanic acid, prepared from Montan wax, was recrystallised from alcohol, and finally from glacial acetic acid until the melting point was constant at 82·5° (uncorr.). The titration value of the acid agreed sharply with that required for an acid of the formula $C_{28}H_{56}O_2$, as stated by Ryan and Dillon (*Sci. Proc. Roy. Dubl. Soc.*, 1909, **12**, 202), not with $C_{29}H_{58}O_2$, as given by Hell (*Zeitsch. angew. Chem.*, 1900, **14**, 556) and by Eisenreich (*Chem. Rev. Fett. Harz-Ind.*, 1909, **16**, 211).

The ketone was prepared as in the case of stearone, a 50 per cent. yield being obtained. It melts at 97°, and is conveniently recrystallised from glacial acetic acid:

0·1124 gave 0·3456 CO_2 and 0·1415 H_2O. C=83·85; H=13·98.
$C_{55}H_{110}O$ requires C=83·96; H=13·97 per cent.

Montanoneoxime melts at 82·5°, and is very sparingly soluble in alcohol, more readily so in ethyl acetate:

0·3371 gave NH_3 equal to 4·2 c.c. $N/10$-HCl. N = 1·74.

$C_{55}H_{111}ON$ requires N = 1·72 per cent.

The *alcohol* obtained by reduction of montanone melts at 101°; the corresponding *acetate* melts at 66°.

Melissone.

The melissic acid was prepared from New Zealand beeswax, and was separated from the cerotic acid by means of the very sparing solubility of sodium melissate in hot 95 per cent. alcohol, in which solvent sodium cerotate is rather easily soluble. The acid melted at 88·5° (uncorr.).

The ketone was prepared by heating the acid with metallic iron for two hours at 370°; the yield was 47 per cent. of that demanded by theory.

Melissone melts at 99·5°, is practically insoluble in boiling absolute alcohol, but may be conveniently recrystallised from amyl alcohol or glacial acetic acid:

0·0804 gave 0·2489 CO_2 and 0·1018 H_2O. C = 84·32; H = 14·06.

$C_{59}H_{118}O$ requires C = 84·08; H = 14·01 per cent.

Schwalbe (*Diss.*, Tübingen) observed a ketone melting at 97—99° amongst the products of the soda-lime fusion of myricyl alcohol from beeswax.

Melissoneoxime melts at 84°.

Oleone, $C_{35}H_{66}O$.

According to Beilstein (Vol. I., p. 1006) no ketones have hitherto been prepared from the unsaturated acids, $C_nH_{2n-2}O_2$. In Watts's Dictionary (Vol. IV., pp. 193 and 196) it is stated that Bussy obtained a neutral, oily liquid by distilling oleic acid with lime, and that he regarded this as oleone. Attempts to prepare oleone by the interaction of oleic acid and phosphoric oxide were unsuccessful, a viscid tar resulting, from which no definite compounds could be extracted by organic solvents. Oleone can, however, be isolated from the distillation products of barium oleate, and more readily from the reaction product of iron with oleic acid. It is also present in the fractions of highest boiling point of commercial oleic acid.

I. Forty grams of barium oleate (Found, Ba = 19·4. Calc., Ba = 19·6 per cent.), recrystallised from a mixture of benzene and alcohol (Farnsteiner, *Zeitsch. Nahr. Genussm*, 1899, **2**, 1), were

heated in a flask immersed in a bath of molten solder. A current of hydrogen was passed into the flask throughout operation, and the pressure was kept below 100 mm. A similar to that used by Young (Trans., 1891, **59**, 623) was to remove the volatile products as rapidly as possible. A first appeared at 280°/25 mm., and was pale yellow and As the temperature rose, the distillate became darker and viscous, and the pressure in the apparatus rose. Distillation and the pressure again fell before a temperature of attained. The total distillate was a reddish-brown, viscous showing a green fluorescence. A small quantity of separated on keeping, and a further crop was obtained by tionating the crude distillate under diminished pressure and the fraction distilling between 280° and 330°/5—10 mm. The weight of crystals was only 2 per cent. of that demanded by for the production of oleone from the barium salt.

After repeated crystallisation from alcohol the substance at 59°:

0·1062 gave 0·3252 CO_2 and 0·1260 H_2O. C = 83·3; H = 13·1.

By ebullioscopic method in alcohol: Found, M.W. = 492 and

$C_{35}H_{66}O$ requires C = 83·66; H = 13·14 per cent. M.W. = 502.

The bromine absorption in chloroform solution after twelve was 62·1 per cent. The absorption of four atoms of requires 63·8 per cent.

It is, of course, possible that in the formation of this oleone the position of the ethylene linkings may have changed from the positions occupied in the oleic acid.

It is not a little remarkable that the distillate boiling at 280—330°, from which the oleone crystals have been removed as far as possible by cooling and filtration, still has almost the same composition as the crystals themselves. (Found, C = ; H = 13·0.) This calls to mind an observation by Miller and Tschitschkin (*Annalen*, 1899, **307**, 375) that the distillate from the calcium salt of azelaic acid yields a fraction boiling at 180—, the analysis of which agrees with that required for *cyclo*octanone but the existence of this compound could only be proved in the fractions boiling above 200°.

II. *Preparation of Oleone by the Interaction of Iron and Oleic Acid.*—One gram of oleic acid prepared from the commercial acid by repeated rectification in a vacuum and removal of saturated fatty acids by freezing, and 5 grams of practically pure oleic acid (prepared from olive oil, solidifying completely at 14°, and yielding a lead salt completely soluble in ether) were separately heated with one-tenth of their weights of powdered and sifted cast-iron turnings

evolution of carbon dioxide began at 240°. The mixture was slowly heated to 340°, and this temperature maintained for two hours; much frothing occurred towards the end of the reaction. After removal of iron and acidic substances, the semi-solid product was crystallised several times from alcohol and acetic acid until the melting point was constant at 59·5°. The yield in each case was [illegible] per cent. of the oleic acid taken:

0·1089 gave 0·3335 CO_2 and 0·1332 H_2O. C = 83·5; H = 13·6.

$C_{35}H_{66}O$ requires C = 83·6; H = 13·1 per cent.

From oleic acid heated to 340° for two hours in the absence of iron no oleone could be isolated.

III. *Isolation of Oleone from Commercial Oleic Acid.*—Since commercial olein is prepared by the steam distillation of crude stearin from cast-iron retorts, the temperature in which frequently exceeds 300°, the presence of oleone is to be expected in commercial oleic acid. By the kindness of the directors and manager (Mr. Bull) of the New Zealand Candle Co. we have been supplied with samples taken during the redistillation of 2 tons of commercial olein, an operation extending over five hours.

The fractions collected during the first four hours distilled almost completely below 270°/50 mm. The portions passing over during the last fifteen minutes were filtered from solids, and only began to boil at 270°/50 mm.; a large portion boiled above 300°/25 mm.

Oleone was obtained from these higher fractions by dissolving in a large volume of alcohol and neutralising with sodium hydroxide, which caused the separation of an oil insoluble in the soap solution. This oil on keeping deposited crystals, which melted at 59° after repeated crystallisation from alcohol and acetic acid.

When prepared by any of these methods *oleone* is a colourless substance, crystallising from alcohol or acetic acid in hair-like needles. It is sparingly soluble, even in boiling alcohol, more readily so in ether, ethyl acetate, glacial acetic acid, or chloroform.

Oleoneoxime melts at 31°, and is readily soluble in alcohol:

0·1334 gave 2·9 c.c. N_2 at N.T.P. N = 2·73.

$C_{35}H_{67}ON$ requires N = 2·70 per cent.

Reduction of Oleone to Pentatriacontane.—0·5 Gram of oleone was warmed with phosphorus pentachloride, and the product subsequently reduced with hydriodic acid and phosphorus at 240°. The resulting hydrocarbon was recrystallised from ether, and melted at 73°. (Found, C = 85·8; H = 14·8. Calc., C = 85·3; H = 14·6 per cent.) Pentatriacontane melts at 74·7° (Krafft, *Ber.*, 1882, **15**, 1715).

Elaidone.

Two grams of pure elaidic acid were heated with iron under similar conditions to those employed for the preparation of oleone. The elaidone was recrystallised from alcohol, and melted at [illegible]. The yield was only 15 per cent. when the maximum temperature employed was 320°; a larger yield was obtained in an experiment in which the maximum temperature was 350°, but the ketone produced at the higher temperature was not readily brought to a sharp melting point by recrystallisation:

Found: C=83·33; H=13·27.

$C_{35}H_{66}O$ requires C=83·62; H=13·14 per cent.

Elaidoneoxime crystallises from alcohol in long needles, which melt at 32°; it is more readily soluble than the oxime of oleone.

0·3678 gave NH_3 equal to 7·8 c.c. *N*/10-HCl. N=2·96.

$C_{35}H_{67}ON$ requires N=2·71 per cent.

Brassidone.

This was prepared from brassidic acid and metallic iron, and melts at 80°. The yield at 280° was 20 per cent., at 320° 50 per cent., of the acid employed. The compound is readily soluble in hot alcohol:

0·1237 gave 0·3787 CO_2 and 0·1495 H_2O. C=83·42; H=13·4[illegible].

$C_{43}H_{82}O$ requires C=84·03; H=13·33 per cent.

Brassidoneoxime melts at 51°:

0·3078 gave NH_3 equal to 4·6 c.c. *N*/10-HCl. N=2·19.

$C_{43}H_{83}ON$ requires N=2·22 per cent.

Action of Iron on Erucic Acid.

Carefully purified eruric acid was heated with powdered iron turnings for three hours at 300—320°. The resulting neutral compound, even after repeated recrystallisation from a variety of solvents, melted at 50—60°, although the analytical numbers agreed with those required for erucicone. (Found, C=83·88; H=13·[illegible]. $C_{43}H_{82}O$ requires C=84·04; H=13·33 per cent.) From the products of distillation of barium erucate under diminished pressure a similar product of indefinite melting point was obtained.

The result would be readily explained if, during the process of heating, a portion of the erucic acid were changed into any of the numerous possible isomerides, so that the ultimate product would be a mixture of isomeric ketones.

Some support in favour of this view is given by the observation

but a sample of the same erucic acid when heated alone for two hours at 280—300° yielded a small quantity of an acid melting at about 50°. The original erucic acid melted at 34°.

The expenses of this investigation have been defrayed by a grant from the Research Scholarship Fund of the Government of New Zealand.

VICTORIA COLLEGE,
WELLINGTON, N.Z.

CCLIV.—*The Separation of Mixtures of Organic Acids by Partial Esterification.*

By JOHN JOSEPH SUDBOROUGH and EBENEZER REES THOMAS.

THE difference between the esterification constant of an $\alpha\beta$-unsaturated acid and its saturated analogue, and between the constants of corresponding $\alpha\beta$- and $\beta\gamma$-acids, and also $\alpha\beta$- and $\gamma\delta$-acids (Trans., 1905, **87**, 1840; 1907, **91**, 1033; 1909, **95**, 315, 975), suggested that possibly mixtures of those acids might be separated by partial esterification. It was found that under specific conditions a separation is brought about by one treatment with alcohol and hydrogen chloride, that the method is perfectly general, and that it can be used whether the composition of the mixture is known or not.

For any such mixture of acids the following general method may be used. The mixture is treated with $0{\cdot}22N$-ethyl-alcoholic hydrogen chloride, when the more readily esterified acid has $E^{15°}_{MeOH}$ about 40. When it is less, the strength of the hydrogen chloride must be rather more than $0{\cdot}22 \times 40 \times N/E'$ (where E' is the esterification constant of the more readily esterified acid in the mixture). About twenty-five to thirty times the amount of alcohol required to combine with the weight of the more readily esterified acid present must be taken. When the composition of the mixture is unknown, it may be regarded as all more readily esterifiable acid. The solution is left at about 20° for five hours or longer,* and then poured into

* With acids of $E^{15°}_{MeOH}$ about 80 a shorter time will suffice. In all cases if left considerably longer than the exact time required, very little difference will be made. In one experiment where four and a-half hours would have been a suitable period, the mixture was left for seventeen and a-half hours and a good separation was obtained (Expt. 1).

about four times its volume of water; the liquid is made slightly alkaline with sodium carbonate, the ester extracted with ether, the extract washed, dried, and distilled, and the ester hydrolysed. The acid may be obtained either by acidifying the alkaline liquid and extracting with ether, or, where insoluble in water, by precipitation. In some cases it may be convenient to obtain the greater part by precipitation, the remainder being extracted from the filtrate with ether.

In working out the conditions, preliminary experiments were carried out, 1 c.c. of the solution being titrated from time to time with standard alkali. Where the E^{15}_{MeOH} of the acids present in the mixture is unknown, the conditions may be found in this way.

The method has been used for:

A. *Separation of αβ-Unsaturated Acids from their Saturated Analogues.*

i. *Cinnamic and β-Phenylpropionic Acids* (compare experiments 1—6).—The method is of interest in this case in view of the fact that in the preparation of β-phenylpropionic acid by the reduction of cinnamic acid, the reduction is seldom complete, and the resulting product is somewhat difficult to purify by recrystallisation.

ii. *Crotonic and Butyric Acids* (compare experiments 7 and 8).

iii. *Dimethylacrylic and* iso*Valeric Acids* (compare experiments 9 and 10).

B. *Separation of Mixtures of αβ- and βγ-Unsaturated Acids*

The method is of interest in two special cases:

i. Where, as in the case of β-ethylacrylic and ethylidenepropionic acids, a mixture of the acids is produced during their preparation. (For separation see experiments 13 and 14.)

ii. When a mixture of the two acids is obtained by boiling the βγ-acid for twenty to fifty hours with excess of sodium hydroxide (Fittig, *Annalen*, 1894, **283**, 51), for example, hydrosorbic and αβ-hexenoic acids. (For separation see experiments 15 and 16.)

A mixture of cinnamic acid and phenyl*iso*crotonic acid was also separated by this method (compare experiments 11 and 12).

The method at present in use for the separation of αβ- and βγ-unsaturated acids is that described by Fittig (*loc. cit.*). With this method (i) considerable difficulty is experienced in working it. Fittig states (*loc. cit.*), "dass sie in anderen Händen nicht immer zu so glatten Resultaten geführt hat." Several experiments on the purification of αβ-pentenoic acid by Fittig's method were carried

but by the authors (Trans., 1907, **91**, 1035), and in these cases very poor yields were obtained, although great care was taken as to conditions. The method here described presents none of these difficulties, and one esterification is sufficient to give a good separation, whilst three treatments with sulphuric acid are necessary in order to obtain the $\alpha\beta$-acid pure.

(ii) All the $\beta\gamma$-acid is lost in the form of the γ-lactone. In the case of hydrosorbic acid, the yield of crude $\alpha\beta$-acid is never more than 30 per cent. of the weight of hydrosorbic acid used (*Annalen*, 1894, **283**, 119), 70 per cent. being thus practically destroyed. In the partial esterification method the only appreciable loss is due to the inevitable formation of hydroxy-acid—about 25 per cent. of the weight of hydrosorbic acid used.

(iii) It has been shown by Fichter (*Ber.*, 1909, **42**, 4707) that β-methyl-Δ^{α}-pentenoic acid is quantitatively transformed into lactone under the conditions described by Fittig for the purification of $\alpha\beta$-acids. They were therefore unable to determine whether β-methyl-Δ^{β}-pentenoic acid was transformed into the Δ^{α}-acid or not by boiling with sodium hydroxide solution. It is hoped that the method described in this paper may be of some use in deciding this point.

C. *Separation of $\alpha\beta$- and $\gamma\delta$-Acids.*

A mixture of δ-phenyl-Δ^{α}- and Δ^{γ}-pentenoic acids was separated in this way (compare experiment 17).

Experimental.

Experiment 1.—*Cinnamic and β-Phenylpropionic Acids* (preliminary).—Two grams of cinnamic acid (recrystallised storax acid) and 2·5 grams of β-phenylpropionic acid (m. p. 47·5°) were dissolved in 15 c.c. of ethyl alcohol, and 5 c.c. of 0·89*N*-solution of hydrogen chloride in ethyl alcohol added, thus giving 20 c.c. of 0·22*N*-hydrogen chloride. In order to watch the course of the reaction, 1 c.c. was removed from time to time, and titrated with 0·0262*N*-barium hydroxide solution, of which by calculation hydrogen chloride required 8·5 c.c.; cinnamic acid, 25·5 c.c.; together 33·5 c.c.; β-phenylpropionic acid, 31 c.c.

After	0·3	0·5	1	1·5	2·5	4	17·5	hours
1 c.c. required	50	48	43·7	40	36	33·7	28	c.c.

From these results it was concluded that presumably nearly all the β-phenylpropionic acid was esterified at the end of about four hours under these conditions, whilst even after leaving for another thirteen hours, only a comparatively small quantity of the cinnamic

acid was esterified. To test this conclusion, the remainder of the alcoholic solution (which had been left for 17·5 hours) was poured into water, and treated as described in the introduction.

1·20 Grams of an acid, melting at about 131°, and 2·08 grams of an ester were obtained. The ester, when hydrolysed, yielded 1·64 grams of an acid melting at 45—47°.

Experiment 2.—Cinnamic and β-Phenylpropionic Acids.—A mixture of 10 grams of each acid was dissolved in 75 c.c. of ethyl alcohol, and 25 c.c. of 0·89*N*-hydrogen chloride in alcohol added. The mixture was left at 18° for about five hours, then poured into 400 c.c. of water, and treated as described in the introduction.

11·99 Grams of ester were obtained, and from the alkaline liquid, after rendering acid and extracting with ether, 9·56 grams of cinnamic acid (m. p. 129·5—132°) were obtained.

The ester was distilled, and 11·20 grams, boiling at 244—246°/772 mm., were collected. This was hydrolysed by means of sodium hydroxide solution, and the acid recovered as before.

8·96 Grams of β-phenylpropionic acid (m. p. 46—47·5°) were obtained. 5·72 Grams of this acid were pressed on filter-paper and then melted at 48—49°. The melting point given by Fittig (*Ber.*, 1890, **23**, 148) is 48·7°. Hence 4·5 grams of this acid were recrystallised from light petroleum (b. p. 35—42°). Three fractions were obtained; (i) 2·73 grams, m. p. 48·5—49·5°; (ii) 1·0 gram, m. p. 48—49°; (iii) 0·76 gram, m. p. 47—48°.

An experiment was subsequently carried out with a mixture (in equal proportions) of these acids, the cinnamic acid being recovered by precipitation.

Experiment 3.—Five grams of each acid were dissolved in [illegible] of ethyl alcohol, 10 c.c. of 1·08*N*-hydrogen chloride in ethyl alcohol were added, and the solution left at 20° for six hours. The mixture was then poured into water, and the ester extracted as before. 5·57 grams of ester, boiling at 243—245°/758 mm., were obtained (=4·83 grams of acid).

The alkaline solution was carefully heated on the steam-bath so as to remove all the ether, cooled, and treated with concentrated hydrochloric acid in excess, when 4·73 grams of cinnamic acid (m. p. 129—131°) were obtained.

Experiments were then conducted to study the conditions for separation when the two acids are not present in equal proportions.

A. *When β-Phenylpropionic Acid is in the Larger Proportion.*

Experiment 4.—Three grams of β-phenylpropionic acid and 1 gram of cinnamic acid were dissolved in 15 c.c. of alcohol, 5 c.c. of 0·89*N*-hydrogen chloride added, and 1 c.c. of the solution

titrated from time to time with 0·0262*N*-barium hydroxide solution, of which by calculation hydrogen chloride requires 8·5 c.c.; cinnamic acid, 12·75 c.c.; together 21·2 c.c.; β-phenylpropionic acid, 13·75 c.c.:

After	1	2	4	5·5	hours
1 c.c. required	32·6	28·3	23·4	22·2	c.c.

The mixture was left for another hour (6·5 hours in all), and then poured into water and treated as before, giving 0·94 gram of cinnamic acid (m. p. 127—129°) and 2·55 grams of β-phenylpropionic acid, which, on pressing on filter-paper, lost a little oil and melted at 48·8—49·4°.

B. *When Cinnamic Acid is in the Larger Proportion.*

Experiment 5.—Three grams of cinnamic acid and 1 gram of β-phenylpropionic acid were dissolved in 15 c.c. of alcohol (solution warmed and cooled), and 5 c.c. of 0·89*N*-alcoholic hydrogen chloride added. One c.c. was removed and titrated as before with 0·0262*N*-barium hydroxide solution, of which hydrogen chloride required 8·5 c.c.; cinnamic acid, 38·0 c.c.; together 46·5 c.c.; β-phenylpropionic acid, 12·6 c.c. After one and 1·5 hours, 1 c.c. required 44·3 and 43·7 c.c. respectively.

At the end of 1·5 hours, the mixture was poured into water and treated as before, and 0·97 gram of ester and 2·72 grams of cinnamic acid (m. p. 126—128·5°) were obtained.

Experiment 6.—*Purification of crude β-phenylpropionic acid, which had been prepared by the reduction of cinnamic acid.*—The crude acid (10·2 grams, m. p. 41—45°) was shaken with alcohol (34 c.c.), and, after settling, the clear liquid was decanted. The flask was rinsed with 10 c.c. of alcohol, which was filtered and added to the solution (weight of insoluble residue = 0·10 gram). 1·08*N*-Alcoholic hydrogen chloride (25 c.c.) was then added, and the mixture left at 20° for about nine hours. It was poured into water, and treated as before. The ester was distilled, and 10·2 grams of ester (b. p. 243—246°/758 mm.) were obtained (= 8·5 grams of acid).

The acid impurity was precipitated from the solution of the sodium salt with hydrochloric acid, collected, washed with water, and dried, when 1·30 grams of cinnamic acid (m. p. 128·5—130°) were obtained.

Separation of Crotonic and Butyric Acid.

Crotonic acid ($E^{15}_{MeOH} = 1·28$), melting at 71—71·4°, and butyric acid ($E^{15}_{MeOH} = 41·63$), boiling at 164—165°, were used.

Experiment 7 (preliminary).—A mixture of 2 grams of each acid was dissolved in 15 c.c. of alcohol, and 5 c.c. of 0·89*N*-alcoholic hydrogen chloride were added. 1 C.c. of the mixture was titrated with 0·0262*N*-barium hydroxide solution, of which hydrogen chloride requires 8·5 c.c.; crotonic acid, 45·0 c.c.; together 53·5 c.c.; butyric acid, 44 c.c. After 1, 2, and 4·5 hours, 1 c.c. required 65, 60, and 51·6 c.c. respectively.

At the end of 4·5 hours the mixture was poured into water and treated as before. 1·69 Grams of crotonic acid (m. p. [illegible]) were obtained. Owing to its extreme volatility, no constant weight of the ester could be observed. The conditions for the separation of these two acids are therefore exactly similar to those used for cinnamic and β-phenylpropionic acids, except that precautions must be taken to avoid loss of ester by volatilisation.

Experiment 8.—Ten grams of each acid were mixed and dissolved in 80 c.c. of alcohol, and 21 c.c. of 1·08*N*-alcoholic hydrogen chloride were added. The mixture was left at 18° for nearly four and a-half hours, poured into water, and neutralised as before; it was then extracted three times with ether, and the ethereal extract washed three times with one-third its volume of water and dried. The acid was obtained in a similar manner on acidifying with hydrochloric acid and extracting with ether.

To avoid loss of ethyl butyrate by volatilisation with the ether vapour, the residue was distilled very slowly from a small distillation flask with a comparatively long neck. A constriction was made at the lower end of the neck, which was filled with glass beads, and a tube for the introduction of more of the liquid passed through the beads and was closed by rubber and a pinchcock at the upper end. Ten grams of ethyl butyrate (b. p. 120—121°/773 mm.) were obtained.

The crotonic acid was distilled and left in a desiccator. [illegible] Grams of acid, melting at about 61°, were obtained. 2·6 Grams were recrystallised from light petroleum (b. p. 40—60°), and gave 1 gram melting at 71—71·2°, 0·9 gram melting at 69·5—70°, and 0·45 gram melting at 67—69°.

Separation of Dimethylacrylic and iso*Valeric Acids.*

Dimethylacrylic acid ($E^{15^\circ}_{MeOH}$ = 0·285, m. p. 67·8—68°), prepared by Barbier and Leser's method (*Bull. Soc. chim.*, 1905, [iii], 33, 815) from mesityl oxide and sodium hypochlorite, and *iso*valeric acid ($E^{15^\circ}_{MeOH}$ = 12·3, b. p. 174·5—175·1°/740 mm.) were used in the experiment.

Experiment 9 (preliminary).—As the esterification constants of these acids are approximately one-quarter of those of cinnamic and

β-phenylpropionic acids, it was thought advisable to use alcoholic hydrogen chloride four times as strong as that used in the previous experiments, the rate of esterification being proportional to the strength of the hydrogen chloride. Hence a mixture of 2 grams of dimethylacrylic acid and 2·3 grams of *iso*valeric acid was dissolved in 10 c.c. of alcohol, and 15 c.c. of 1·46*N*-alcoholic hydrogen chloride were added. One c.c. of this solution was titrated against 0·0313*N*-barium hydroxide solution, of which hydrogen chloride required 28·2 c.c.; dimethylacrylic acid, 25·3 c.c.; together 53·5 c.c.; *iso*valeric acid, 29·1 c.c. After leaving for four and six and a-half hours, 1 c.c. required 57·1 and 53·7 c.c. respectively, thus under these conditions leaving for six and a-half hours will probably bring about a separation.

Experiment 10.—Ten grams of dimethylacrylic acid were dissolved on warming in 20 c.c. of alcohol. The solution was cooled, and 10 grams of *iso*valeric acid were added. To the solution 90 c.c. of 1·08*N*-alcoholic hydrogen chloride were added, and the mixture was left at 20° for six and a-half hours. It was then poured into water and treated as before. The ether was in this case also distilled off very carefully from the ester, and the following fractions were collected: Below 78°; 78—100°; and, of which 9·65 grams were obtained, 133—135°/737 mm. Ether was added to the fraction b. p. 78—100°, which was then treated twice with its own volume of water, the ethereal layer being separated and dried. The fraction b. p. 133—135°/740 mm., obtained on distillation, was added to the former amount of ester obtained; the total weight of pure ester was 11·23 grams. As dimethylacrylic acid is appreciably soluble in water, the solution of the sodium salt was evaporated to a small volume, cooled, and then acidified with hydrochloric acid. The weight of acid obtained was 6·10 grams (m. p. 67·3°), and from the aqueous filtrate was extracted, by means of ether, 3·45 grams, of which 2·12 grams were pressed on a porous plate, yielding 1·90 grams of acid melting at 69°.

Separation of Mixtures of αβ- and βγ-Unsaturated Acids.

Cinnamic Acid and Phenylisocrotonic Acid ($E^{16°}_{MeOH}=86·6$).—Recrystallised storax cinnamic acid and phenyl*iso*crotonic acid (m. p. 86°), prepared from phenylparaconic acid (Trans., 1907, **91**, 1034), were used.

Experiment 11.—A mixture of 2 grams of each acid was dissolved in 20 c.c. of warm alcohol, and the solution cooled; 5 c.c. of 1·08*N*-alcoholic hydrogen chloride were added, and 1 c.c. of the mixture titrated as before with 0·0262*N*-barium hydroxide

solution, of which hydrogen chloride required 8·2 c.c.; cinnamic acid, 20·6 c.c.; together 28·8 c.c.; phenylisocrotonic acid, [illegible] c.c. After 2·6 hours, 1 c.c. required 27·0 c.c. of the alkali, and the mixture was then poured into water and treated as before. [illegible] grams of ethyl phenylisocrotonate were obtained, yielding on hydrolysis 1·81 grams of acid (m. p. 76—79°) and 2·21 grams of cinnamic acid (m. p. 124—127°). Hence for such a mixture under these conditions three hours is probably sufficient.

Experiment 12.—Ten grams of each acid were mixed and dissolved in 80 c.c. of alcohol, and 21 c.c. of 1·08*N*-alcoholic hydrogen chloride added. The mixture was left at 20° for three hours, and then poured into water and treated as before. On evaporating the ether, 10·53 grams of an acid, melting at 125—127°, were obtained, and a faint odour of benzaldehyde was noticed. [illegible] Grams of this acid were neutralised with sodium carbonate solution, and the solution was boiled until the odour of benzaldehyde was no longer perceptible. On acidifying with hydrochloric acid, about 9·2 grams of acid, melting at 131—133°, were obtained.

After removal of ether, the ester was carefully distilled under the ordinary pressure, and 9 grams of a fraction boiling at 281—282°/763 mm. were collected. A further 1·6 grams passed over about this temperature, the small amount of liquid making it difficult to read the temperature accurately. The mercury finally rose to 290°, when the distillation was stopped. Slight decomposition takes place during the distillation, a little tarry residue being left in the flask.

This ester does not appear to have been described, hence its composition was determined:

0·3182 gave 0·8880 CO_2 and 0·2088 H_2O. C = 76·1; H = 7·30.
0·2486 „ 0·6954 CO_2 „ 0·1686 H_2O. C = 76·2; H = 7·53

$C_{12}H_{14}O_2$ requires C = 75·8; H = 7·37 per cent.

The *ethyl phenyl*iso*crotonate* obtained in this way had D^{20} [illegible]

β-*Ethylacrylic and Ethylidenepropionic Acids.*

The mixture of these acids was prepared as before (Trans., 1907, **91**, 1035).

Experiment 13.—From 50 grams of malonic acid, 16 grams of the fraction boiling at 190—205°/756 mm. were collected. This was left in a desiccator overnight, and then tested by titrating a known weight with standard alkali:

0·0976 required 30 c.c. 0·0262*N*-barium hydroxide. Calc., 37·3 c.c.
0·1330 „ 40·65 c.c. „ „ Calc., 50·8 c.c.

Hence this liquid probably contains as impurity some neutral sub-

stance in addition to the two acids. It was purified as follows: The liquid was shaken with a solution of sodium carbonate, and extracted three times with ether, the ethereal solution finally yielding 3 grams of a neutral oil boiling at about 200°.

The alkaline solution was acidified with hydrochloric acid, and extracted with ether as before; 10·5 grams of a fraction boiling at 19-–203° were obtained:

0·0682 required 26·05 c.c. 0·0262*N*-barium hydroxide. Calc., 26·0 c.c.

Hence probably a mixture of β-ethylacrylic and ethylidenepropionic acids was present.

Separation of the Mixture.—Ten grams of the mixture were placed in a flask, and 60 c.c. of alcohol and 15 c.c. of 1·08*N*-alcoholic hydrogen chloride were added. The solution was left at 20° for four and a-half hours, and then poured into water and treated as before. The ether was very slowly distilled from the ethereal solution of the acid, using the glass beads, etc., described in experiment 8.

4·7 Grams of acid, boiling at about 200°, were obtained. Some ether was distilled off from the ethereal solution of the ester, and the remainder kept for treatment with that obtained in experiment 14.

Experiment 14.—The mixture of acids was prepared as before, 16 grams of a fraction boiling at 190—205° being obtained. This was purified as described in experiment 13, and 9·3 grams of acid boiling at 190—203° were obtained:

0·1496 required 55·5 c.c. 0·0262*N*-barium hydroxide. Calc., 57 c.c.
0·0932 „ 34·3 c.c. „ „ Calc., 35·5 c.c.

The mixture therefore contained only 97 per cent. of the acids.

Separation of the Mixture.—Nine grams of the mixture were mixed with 60 c.c. of alcohol, 17 c.c. of 1·08*N*-alcoholic hydrogen chloride added, and the solution left at 20° for four and a half hours. It was then poured into water, and treated exactly as in experiment 13. 4·35 Grams of acid, boiling at 198—201°/ 37 mm. were obtained, and this was added to the 4·7 grams obtained in experiment 13. The mixture, on distillation, gave 3 grams of ethylacrylic acid (b. p. 197—201°/751 mm.). This was placed in a freezing mixture, when the greater part solidified, melting at 5° (Fittig and Mackenzie, *Annalen*, 1894, **283**, 83, give 5—10·5° as the melting point of the pure acid).

The ethereal solution of the ester was mixed with that obtained in experiment 13, and the ether slowly distilled, using a rod-and-disk fractionating column. When nearly all the ether had been

removed, the ester was hydrolysed by means of barium hydroxide solution, and the crystalline barium ethylidenepropionate obtained and weighed.

Four hundred c.c. of barium hydroxide solution (saturated at 15°) were added to the ester, and the whole was boiled in a reflux apparatus for two hours, when apparently complete hydrolysis had taken place. The liquid was extracted once with ether to remove any unhydrolysed ester, and then freed from ether by passing steam through it. Carefully washed carbon dioxide was then passed through the hot solution to precipitate any excess of barium hydroxide, and the solution filtered. On evaporating to a small volume, cooling, and adding alcohol, pearly-white crystals were precipitated. These were removed, washed with alcohol, pressed on a porous plate, and dried in the steam-oven. Weight [illegible] grams.

The solution and washings were evaporated to dryness, and the crystals obtained were treated in the same way as the former fraction: 5·8 grams were obtained, making a total of 11·5 grams of barium ethylidenepropionate (7 grams of acid). As the barium salt of ethylacrylic acid is a gum, the former salt must be almost pure, and, by one esterification, it has been possible to obtain 8·3 grams of pure ethylacrylic acid and 7 grams of pure ethylidene-propionic acid from 19 grams of the mixture.

Transformation of Hydrosorbic Acid into αβ-Hexenoic Acid and Purification of the Mixture Obtained by Partial Esterification.

Hydrosorbic acid was prepared as described by Sudborough and Thomas (Trans., 1910, **97**, 2450) by the reduction of sorbic acid in alkaline solution by means of 3 per cent. sodium amalgam. 13·7 Grams of the acid were treated as described by Fittig (*Annalen*, 1894, **283**, 117) with 266 c.c. of 20 per cent. sodium hydroxide solution, the solution being boiled under a reflux condenser for thirty-five hours: 10·27 grams of a yellow oil, presumably a mixture of αβ-hexenoic and hydrosorbic acids, were obtained by steam distillation, and 3·1 grams of hydroxy-acid from the residue. The αβ-hexenoic and hydrosorbic acids were separated as follows.

Experiment 15.—10·27 Grams of the mixture were treated with 60 c.c. of alcohol and 20 c.c. of 1·02*N*-alcoholic hydrogen chloride, and left for five and a-half hours at 20°. The mixture was then separated by exactly the same method as that adopted in the previous experiments, the ester being very carefully freed from ether. Nine grams of ester, boiling at 170—172°/762 mm., were obtained. The aqueous solution was heated on a steam-bath to

remove ether and alcohol, and then evaporated to a small volume. On cooling, the $\alpha\beta$-hexenoic acid was precipitated by addition of hydrochloric acid in excess, when 0·9 gram was obtained, which melted at 32·1—32·3° (Fittig gives 32·7—33·1° as the melting point of the pure acid). The aqueous filtrate was extracted three times with ether, the ethereal extract yielding 1·7 grams of acid, nearly all of which solidified—a trace of oil being observed.

Experiment 16.—The 9·0 grams of ester were first carefully hydrolysed and then boiled with sodium hydroxide as before for thirty-five hours. 5·83 Grams of the mixture of $\alpha\beta$-hexenoic and hydrosorbic acids were obtained, and to this 34 c.c. of alcohol and 14 c.c. of 0·947*N*-alcoholic hydrogen chloride were added, and the solution left for five and a-half hours. It was then poured into water, and treated as before, except that, the acid being only a small quantity, the solution of the sodium salt was evaporated so as to precipitate all the acid. 5·55 Grams of ester (b. p. 170—172°) and 0·4 gram of acid (m. p. 27·5—28·5°) were obtained.

Separation of $\alpha\beta$- and $\gamma\delta$-Unsaturated Acids.

$\alpha\delta$-Hydrocinnamylidenemalonic acid,

$$CH_2Ph{\cdot}CH{:}CH{\cdot}CH(CO_2H)_2,$$

was prepared as described by Riiber (*Ber.*, 1904, **37**, 2274; compare also Trans., 1910, **97**, 2452).

To obtain the corresponding substituted acetic acid, this acid was boiled with water, as described by Riiber (*Ber.*, 1905, **38**, 2746). The oily δ-phenyl-Δ^{β}-pentenoic acid obtained did not crystallise from light petroleum as stated by Riiber, and gave 188 as the mean of two determinations of its equivalent weight (δ-phenyl-Δ^{β}-pentenoic acid = 176, corresponding hydroxy-acid = 194). Apparently there was some hydroxy-acid present. The oil was, however, without further purification used for treatment with sodium hydroxide solution, as described by Riiber, for conversion into a mixture of the isomeric $\alpha\beta$-, $\beta\gamma$-, and $\gamma\delta$-acids with some hydroxy-acids; 13·2 grams of such a mixture were obtained, giving 4·1 grams of insoluble hydroxy-acid (m. p. 129—130°) and 8·7 grams of a mixture of $\alpha\beta$-, $\beta\gamma$, and $\gamma\delta$-acids on treatment with boiling carbon disulphide.

The mixture of unsaturated acids was pressed on a porous plate, the oily $\beta\gamma$-acid being absorbed, and 5·5 grams of a mixture of $\alpha\beta$- and $\gamma\delta$-acids obtained. This was dried in a desiccator, and separated as follows.

Experiment 17.—Thirty-six c.c. of alcohol and 12 c.c. of 0·947*N*-alcoholic hydrogen chloride were added to the 5·5 grams

of the mixture, the solution left for five and a-half hours at [illegible] and then poured into water and treated as before, 4·03 grams of ester being obtained.

The alkaline aqueous solution was evaporated to a small volume, acidified with hydrochloric acid, the precipitated acid removed, and the filtrate extracted with ether: 1·75 grams of the αβ-acid (m. p. 99—101°; Riiber gives 104°) were obtained by precipitation, whilst 0·12 gram remained in the flask after removal of ether from the ethereal extract.

The 4·03 grams of ester were hydrolysed, and the acid recovered in exactly the same way as that used for the αβ-acid: 3·15 grams of acid (m. p. 79—82°; Sudborough and Thomas give 91—[illegible]) were obtained by precipitation, and 0·4 gram from the ethereal extract. The latter contained a little oil, and when pressed on a porous plate melted at 126—128°; it was therefore probably the hydroxy-acid.

2·9 Grams of the acid (m. p. 79—82°) were recrystallised from light petroleum (b. p. 60—80°), a small quantity of insoluble matter being removed, and 1·75 grams of crystals, melting at 88—89°, and 0·85 gram, melting at 84—86°, were obtained.

THE EDWARD DAVIES CHEMICAL LABORATORIES,
UNIVERSITY COLLEGE OF WALES,
ABERYSTWYTH.

CCLV.—*The Absorption Spectra of Various Iodine Derivatives of Benzene and Toluene as Vapours in Solution, and in Thin Films.*

By JOHN EDWARD PURVIS.

THE author has previously given accounts of investigations of the ultraviolet absorption spectra of the vapours of chloro- and bromo-benzene, of *o*- and *m*-dichloro- and dibromo-benzene, and of *o*- and *m*-chloro- and bromo-toluene (this vol., pp. 811 and 1699).

The investigation has been continued with iodobenzene, *o*- and *m*-iodotoluene, and *o*- and *m*-di-iodobenzene. The apparatus employed and the general experimental method have been described before (*loc. cit.*).

Vapours.—Iodobenzene.

TABLE I.

The absorption spectrum of iodobenzene in a 1-dcm. tube has been studied by Pauer (*Ann. Phys. Chem.*, 1897, [iii], **61**, 363).

who observed two bands at λ 2625 and λ 2620. The author has studied the vapour of the substance at various temperatures and pressures in a column 200 mm. long and 20 mm. diameter. No such bands were observed, and the following table describes the absorption under the varying conditions of temperature and pressure

	Pressure in mm.	
[illegible]	767	The rays were transmitted to the Cd line 2313, which was fairly strong
[illegible]	811	The rays were transmitted to the Cd line 2329; the Cd lines 2321 and 2313 were just visible
45	837	The rays were transmitted to about λ 2630, where they gradually faded away; the Cd line 2573 was weak, and the rays were then feebly transmitted from about λ 2500 to about λ 2350, where they were again absorbed.
[illegible]	867	The rays were transmitted to about λ 2700
75	897	The rays were transmitted to about λ 2850; the Cd line 2748 was just visible
[illegible]	927	The rays were transmitted to about λ 2930, and the Cd line 2881 was just visible

A careful search was made for the two bands described by Pauer, but none were found. The vapour showed no absorption bands at any of the temperatures and pressures employed, whereas a considerable number of absorption bands were found in the vapours of the corresponding chlorine and bromine compounds (*loc. cit.*).

The absorption phenomena of the vapours of *o*- and *m*-iodotoluene were also studied in a column 200 mm. long and 20 mm. diameter, and no bands were observed. The following tables (II and III) describe the phenomena observed at various temperatures and pressures.

o-Iodotoluene.

TABLE II.

t.	Pressure in mm.	
17°	766	The rays were transmitted to about λ 2300; the Cd line 2288 was just visible
30	810	The rays were transmitted to about λ 2310
45	836	The rays were transmitted to about λ 2340; the Cd lines 2329 and 2321 were just visible
60	866	The rays were transmitted to about λ 2400; they were very weak from about λ 2650 to λ 2500; the Cd line 2573 was not very strongly marked
75	896	The rays were transmitted to about λ 2800; the Cd line 2748 was very weak
90	926	The rays were transmitted to about λ 2900; the Cd line 2837 was just visible

m-*Iodotoluene.*

TABLE III.

$t°$.	Pressure in mm.	
17°	763	The rays were transmitted to about λ 2330; the Cd lines 2329, 2321, and 2313 were visible
30	807	The rays were transmitted to about λ 2330; the Cd lines 2329 and 2321 were visible
45	833	The rays were transmitted to about λ 2360
60	863	The rays were transmitted to about λ 2670; the Cd line 2573 was only moderately strong
75	893	The rays were transmitted to about λ 2830; the Cd line 2748 was only moderately strong
90	923	The rays were transmitted to about λ 2900; the Cd line 2837 was just visible

Like the vapour of *o*-iodotoluene, the vapour of *m*-iodotoluene exhibited no absorption bands at any of the above temperatures and pressures, whereas a considerable number of bands were found in the vapours of the corresponding chlorine and bromine compounds (*loc. cit.*).

As regards the vapours of the two solids *o*- and *m*-di-iodobenzene, the melting points of which are 27° and 40° respectively, each substance was introduced in the 200 mm. tube which was placed in the water-bath at 45°. Two series of experiments were taken, one under a constant diminished pressure and at varying temperatures, and the other at varying pressures and temperatures. No bands were observed, and the tables IV, V, and VI describe the phenomena observed.

o-Di-iodobenzene.

TABLE IV.

The following table describes the phenomena observed in the vapour of *o*-di-iodobenzene at varying temperatures and constant pressure.

$t°$.	Pressure in mm.	
47	17	The rays were transmitted to λ 2250; the Cd lines 2265, 2194, and 2144 were visible
60	17	The rays were transmitted to λ 2250; the Cd lines 2265 and 2194 were visible
75	17	The rays were transmitted to about λ 2380; the Cd lines 2329 to 2265 were visible
90	17	The rays were transmitted to λ 2410; the Cd lines 2329 to 2265 were visible, but weaker than at 75°.

TABLE V.

The following table describes the phenomena observed in the vapour of *o*-di-iodobenzene at varying temperatures and pressures.

t°.	Pressure in mm.	
45	757	The rays were transmitted to about λ 2400 ; the Cd lines from 2329 to 2194 were visible
60	857	The rays were transmitted to λ 2550 ; the Cd lines 2329 to 2265 were very weak
75	887	The rays were transmitted to λ 2650 ; the Cd line 2573 was weak
90	917	The rays were transmitted to λ 2850 ; the Cd line 2748 was weak

m-*Di-iodobenzene.*

TABLE VI.

The following table describes the phenomena observed in the vapour of *m*-di-iodobenzene at varying temperatures and pressures.

t°.	Pressure in mm.	
45	757	The rays were transmitted to λ 2240 ; the Cd lines 2194 and 2144 were visible
60	857	The rays were transmitted to λ 2450 ; the Cd lines 2329 to 2265 were weak
75	887	The rays were transmitted to λ 2550
90	917	The rays were transmitted to λ 2650 ; the Cd line 2573 was very weak

That is to say, no absorption bands were observed in the vapours of *o*- and *m*-di-iodobenzene, whereas a considerable number of bands were found in the vapours of the corresponding *o*- and *m*-dichloro- and dibromo-benzenes (*loc. cit.*).

Solutions in Alcohol: Iodobenzene.

TABLE VII.

The absorption spectra of solutions of iodobenzene have been investigated by Pauer (*loc. cit.*), who found no bands. The author has studied the absorption spectra of various strengths of alcoholic solutions of iodobenzene, and table VI describes the phenomena observed.

Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.
$M/10$	2	2820
	10	2980
	20	3050
	30	3080
$M/100$	2	2400
	10	2730
	20	2800
	30	2850
$M/1000$	2	2330
	10	2380
	20	2410
	30	2500

That is to say, no bands were observed in alcoholic solut[illegible] iodobenzene, whereas alcoholic solutions of each of the corre[illegible]ing substances chloro- and bromo-benzenes exhibited seven [illegible] the two most refrangible bands being very weak (*loc. cit.*).

The following table (VIII) describes the absorption of var[illegible] alcoholic solutions of *o*- and *m*-iodotoluene.

TABLE VIII.

o-Iodotoluene.			*m*-Iodotoluene.		
Strength of solution.	Thickness of solution in mm.	Limit of trans-mitted rays. λ.	Strength of solution.	Thickness of solution in mm.	L[illegible] of [illegible] mi[illegible] [illegible]
$M/100$	2	2410	$M/100$	2	[illegible]
	10	2770		10	[illegible]
	20	2820		20	[illegible]
	30	2860		30	[illegible]
$M/1000$	2	2350	$M/1000$	2	[illegible]
	10	2400		10	[illegible]
	20	2420		20	[illegible]
	30	2500		30	[illegible]

No bands of selective absorption were observed in any of th[illegible] solutions, whereas alcoholic solutions of the corresponding ch[illegible] and bromo-toluenes exhibited two wide diffuse bands and a ve[illegible] weak doubtful band on the more refrangible side (*loc. cit.*).

The following table (IX) describes the absorption of vari[illegible] alcoholic solutions of *o*- and *m*-di-iodobenzene.

TABLE IX

o-Di-iodobenzene.			*m*-Di-iodobenzene.		
Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.	Strength of solution.	Thickness of solution in mm.	Limit of transmitted rays. λ.
M/100	2	2750	*M*/100	2	2730
	10	2980		10	2950
	20	3130		20	2990
	30	3240		30	3050
M/1000	2	2480	*M*/1000	2	2420
	10	2550		10	2470
	20	2690		20	2570
	30	2840		30	2750

No bands of selective absorption were observed, whereas alcoholic solutions of each of the corresponding dichloro- and dibromobenzenes showed four well-marked bands (*loc. cit.*); the fourth most refrangible band in each of the dibromobenzenes was very weak and difficult to distinguish.

Liquids in Thin Films.

Each liquid was pressed between two quartz plates, and held rigidly in front of the slit of the spectroscope. The radiant energy of the Cd spark was passed through the thin films for various periods of time varying from one minute to five minutes. As regards the two solids *o*- and *m*-di-iodobenzenes, the melting points of which are 27° and 40° respectively, a few crystals of each substance were placed on one of the quartz plates, which was warmed just to the melting point of the substance, and the other quartz plate was then pressed closely over the liquid. There was no crystallisation of either substance while the absorption was being photographed. The following table gives the limits of the transmitted rays through thin films of the various substances.

TABLE X.

	Time of exposure in in minutes.	Limit of transmitted rays. λ.
Iodobenzene	5	2600
o-Iodotoluene	5	2780
m-Iodotoluene	5	2820
o-Di-iodobenzene	5	2900
m-Di-iodobenzene	5	2850

In no case was any absorption band observed; whereas thin films of the corresponding chloro- and bromo-benzenes showed seven bands, the most refrangible in each case being very weak; the *o*- and

m-chloro- and bromo-toluenes showed two well-marked bands and a doubtful more refrangible third; the *o*- and *m*-dichloro- and -dibromo-benzenes showed three well-marked bands and a doubtful more refrangible fourth; and toluene exhibited three bands (*loc. cit.*).

Results and Conclusions.

The results of the preceding observations prove that in the ultra-violet regions neither the vapours, nor the alcoholic solutions, nor the thin films of the iodine derivatives of benzene or of toluene exhibit any bands of selective absorption, whereas the corresponding chlorine and bromine compounds have a well-marked series of bands under similar physical conditions.

The decrease in the number of vapour bands when the number and weight of the side-chains are increased is analogous to that observed by Hartley in the case of benzene and its homologues (*Phil. Trans.*, 1908, *A*, **208**, 475); for example, the maximum number of bands found in benzene by Hartley was 84, in toluene 22, in ethylbenzene 19, in *o*-xylene 23, in *m*-xylene 41, in *p*-xylene 30, in cymene 9, and in mesitylene 4. In the halogen derivatives the maximum number of bands found by the author (*loc. cit.*) in the vapour of chlorobenzene was 72, in bromobenzene 62, in *o*-dichlorobenzene 29, in *m*-dichlorobenzene 35, in *o*-dibromobenzene 30, in *m*-dibromobenzene 13, in *o*-chlorotoluene 23, in *m*-chlorotoluene 20, in *o*-bromotoluene 15, and in *m*-bromotoluene 19; so that the chief controlling factors are the type, weight, and orientation of the introduced radicles. Now when the heavy iodine atom takes the place of either chlorine or bromine, the bands completely disappear, and there is no selective absorption. Analogous phenomena are observed in the bands of the alcoholic solutions and of the thin films of these various substances. The few broad diffuse bands observed in the solutions and in the thin films of the chlorine and bromine derivatives completely disappear in the solutions and the thin films of the corresponding iodine compounds. At the same time, the differences in the positions where general absorption begins in equimolecular solutions of the ortho- and meta-compounds indicate that the orientation of the side chain is a factor in determining the extent of the general absorption.

In previous communications (*loc. cit.*) the author has suggested an explanation to account for the facts observed in the chlorine and bromine compounds of benzene and toluene; and the phenomena observed in the corresponding iodine compounds appear to support that explanation. The heavy iodine atom is the controlling force, and it damps and dislocates the movements of the atoms of the benzene nucleus as well as the alkyl side-chains, so that the

rhythmical oscillations or vibrations are destroyed, and no selective absorption is possible. The dislocation of the oscillations occurs, not only when the vibrations are restricted, as in the alcoholic solutions and in the thin films, but also in the vapours where the vibrations are not subjected to any external forces except those of variations of temperature and pressure. Besides the mass of the atom, the action of the radiant energy may be a considerable factor in the final result; because each atom will absorb an amount of energy dependent on its intrinsic characters, and this will react on its own vibrations and on the vibrations of the other atoms. The final adjustment, therefore, will depend on the balance of a complex series of disturbances, and the forces which determine these include such factors as the number, the mass, the intrinsic characters, and the orientation of the atoms of both the nucleus and the side-chains; the physical conditions of the vibrating system as vapours or in solution or as liquids at various temperatures and pressures; and on the distribution and reaction of the vibrations consequent on the absorption of the radiant energy by the various oscillating atoms and atomic groups.

The author is engaged in a comparative study of naphthalene and anthracene and their derivatives, the results of which will be submitted later; and he desires to thank again the Government Grant Committee of the Royal Society, by whose assistance the larger portion of the cost of the apparatus was defrayed.

UNIVERSITY CHEMICAL LABORATORY,
CAMBRIDGE.

CCLVI.—*Influence of Double Linking on Optical Activity; Some* n-*Propyl and Allyl Derivatives of Menthol.*

By PERCY FARADAY FRANKLAND and HUGH HENRY O'SULLIVAN.

IN connexion with the problem of ascertaining the influence of double linking on optical activity it has been shown by one of us that both in the substitution of tartramide and of malamide by *n*-propyl and by allyl respectively the resulting *n*-propylamides have higher molecular rotations than the corresponding allylamides (P. Frankland and Twiss, Trans., 1906, **89**, 1854; and P. Frankland and Done, Trans., 1906, **89**, 1861), which is contrary to the generally

accepted rule that unsaturated groupings bring about a higher rotation than the corresponding saturated ones. This rule is based on results obtained in a number of investigations made during the past thirteen years by Tschugaeff (*Centralbl.*, 1898, **69**, I, [illegible]; II., 404; 1902, **73**, II., 1238), Haller, Rupe (for many references to literature see Trans., 1903, **83**, 1351), Hilditch (Trans., 1908, **93**; 1909, **95**, 1910, **97**, 1911, **99**; *Zeitsch. physikal. Chem.*, 1911, **77**, 482), and others.

The present communication contains data obtained in the further investigation of this subject.

The compounds which we have prepared are three pairs of *n*-propyl and allyl derivatives of menthol; they were all liquids, and their rotations were determined at a number of different temperatures between 15° and 100°. Their rotations have also been determined in methyl alcohol solution.

In the following table we have recorded the values for $[M]_D^{20}$ in the liquid state, whilst we have included for comparison the corresponding values for some other *n*-propyl and allyl compounds.

	B. p.	$[M]_D^{20}$ in liquid state.
Menthoxyacetic allylamide,	185—187°/14 mm.	−192·5°
Menthoxyacetic propylamide	188—189°/16 mm.	193·7
Allyl menthoxyacetate	182°/40 mm.	234·4
Propyl menthoxyacetate	172°/26 mm.	234·1
Menthyl allylaminoacetate	155—157°/17 mm.	160·5
Menthyl propylaminoacetate	159—161°/17 mm.	158·3
Menthyl allyl ether *	—	$[M]_D^{18}$ −192·5
Menthyl propyl ether †	—	182·5

	M. p.	$[M]_D^{20}$ in pyridine solution.
Tartaric allylamide ‡	183°	+251°
Tartaric propylamide ‡	216	+289
Malic allylamide §	117·5	− 72·7
Malic propylamide §	126	90·5

* Haller and Marsch (*Compt. rend.*, 1904, **138**, 1665).

† Tschugaeff (*Centralbl.*, 1902, II, 1238).

‡ Frankland and Twiss (*loc. cit.*).

§ Frankland and Done (*loc. cit.*).

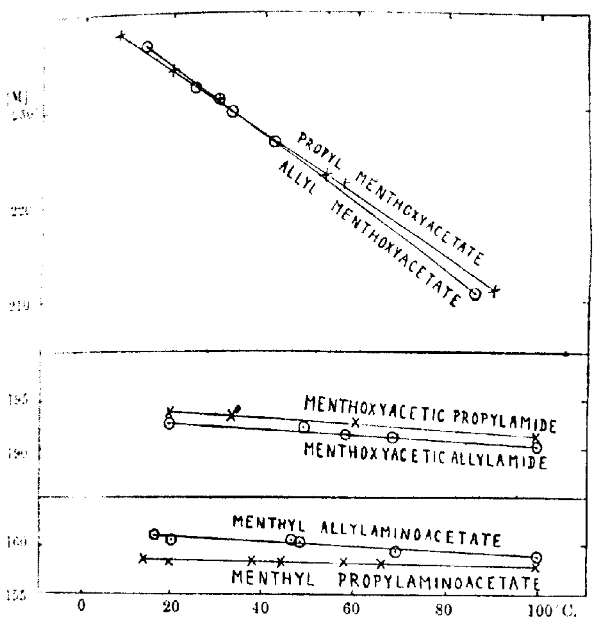
In the case of the amides of menthoxyacetic acid the allyl compound is seen to have the lower molecular rotation, but the difference is very small. This difference is practically the same over the range of temperature at which the observations were made. In this case the double linking diminishes the rotatory power, and agrees in this respect with the results obtained with the tartaric and malic amides.

The allyl and propyl esters of menthoxyacetic acid have practically identical molecular rotations at 20°, but whilst below 35° the

rotation of the allyl is very slightly in excess of that of the propyl compound, above that temperature the relation is reversed (see diagram).

In the case of the next pair, menthyl allylaminoacetate and propylaminoacetate, the allyl compound has slightly the higher molecular rotation throughout the whole range of temperature over which the observations were made.

Molecular rotation curves of the six compounds.



The results recorded in this paper lead to some general considerations:

(1) The extremely small differences between the molecular rotations of the pairs of allyl and propyl compounds described may be accounted for by the great distance of the unsaturated grouping in the allyl from the nearest asymmetric carbon atom in the menthyl radicle; thus, in menthoxyacetic allylamide, in allyl menthoxyacetate, and in menthylallylaminoacetate there are, in each case, *five atoms intervening between the unsaturated carbon atom of the allyl and the nearest asymmetric carbon atom of the menthyl.* That a constitutional change (such as passing from allyl to propyl)

made at such a great distance from the asymmetric carbon atom should have but little effect on the rotation is in accordance with the conclusions arrived at by P. Frankland and MacGregor (Trans., 1896, **69**, 121), and since confirmed by many other workers.

(2) Much greater differences in the molecular rotations of the following pairs of allyl and propyl compounds have been observed:

Liquid state.	Menthyl allyl ether	$[M]_D^{19}$	$-192·5°$	Difference 10°
	Menthyl propyl ether	$[M]_D^{19}$	$-182·5°$	

In the menthylallyl ether there are only two atoms intervening between the unsaturated carbon atom of the allyl and the nearest asymmetric carbon atom of the menthyl group.

Pyridine solution.	Tartaric allylamide	$[M]_D^{20}$	$+251°$	Difference $=38/2=19°$
	Tartaric propylamide	$[M]_D^{20}$	$+289°$	
	Malic allylamide	$[M]_D^{20}$	$-72·7°$	Difference $=17·8°$
	Malic propylamide	$[M]_D^{20}$	$-90·5°$	

In each of the two allyl compounds there are 3 atoms intervening between the unsaturated carbon of one allyl group and 4 atoms between that of the other allyl group and the asymmetric carbon atom of the tartaric and malic radicles respectively.

We do not think that any comparisons between the quantitative differences obtained in the case of the menthyl ethers on the one hand, and the amides of tartaric and malic acids respectively on the other, would be justifiable, first, because of the entirely different nature of the asymmetric nuclei concerned in the two cases, and secondly, because the rotations of the menthyl ethers were determined in the liquid state, whilst those of the tartaric and malic amides were taken in solution, and a great variation was found in the differences between the rotations of the propyl- and allyl-amides according to the particular solvent employed (pyridine, methyl alcohol, water, and glacial acetic acid) (see Frankland and Twiss, Trans., 1906, **89**, 1853, and Frankland and Done, Trans., 1906, **89**, 1860).

(3) It will be seen that the menthoxyacetic grouping gives rise to a much higher molecular rotation than the menthyl aminoacetate grouping, and that the propyl and allyl esters of menthoxyacetic acid again have higher rotations than the corresponding propyl- and allyl-amides.

(4) In this connexion the following relations are worthy of note:

	$[M]_D^{20}$.
Menthyl allylaminoacetate	$-160·5$
Menthyl propylaminoacetate	158·3
Menthyl propionate *	160·2
"Normal constant of the menthyl homologous fatty esters" *	157·5
Menthyl phenylpropionate *	161·9

* Tschugaeff.

Thus, such profound differences in constitution as exist between the fatty acids on the one hand and the substituted amino-fatty acids on the other are attended with practically no alteration in the molecular rotation. These changes in constitution are ineffective, because occurring at a point remote from the asymmetric grouping.

(5) Again, the greater rotatory effect of the menthyl ether than of the menthyl ester grouping which we have found is in accordance with similar results obtained by Tschugaeff, thus:

	$[M]_D^{20}$.
Menthyl methyl ether	$-162.6°$
Menthyl ethyl ether	179·0
Menthyl propyl ether	182·5
Menthyl benzyl ether	232·7
Menthyl formate	146·3
Menthyl acetate	157·8
Menthyl propionate	160·2
Menthyl n-butyrate	156·9
Menthyl n-nonoate	157·3
Menthoxyacetic allylamide	192·5
Menthoxyacetic propylamide	193·7
Menthoxyacetic allyl ester	234·4
Menthoxyacetic propyl ester	234·1
Menthyl allylaminoacetate	160·5
Menthyl propylaminoacetate	158·3

From the above figures it will be seen incidentally that the acetic allyl ester and acetic propyl ester groupings have almost exactly the same rotatory effect as is exerted by the benzyl radicle in the series of menthyl ethers.

This greater rotatory effect of the menthyl ether than of the menthyl ester grouping is in reality a further illustration of what has been pointed out by Purdie and Irvine (Trans., 1901, **79**, 964) in respect of ethyl malate, ethyl monomethoxysuccinate, and ethyl acetylmalate on the one hand, and in respect of ethyl tartrate, ethyl dimethoxysuccinate, and ethyl diacetyltartrate on the other, and by P. Frankland and Gebhard (Trans., 1905, **87**, 864) in respect of the alkyl glycerates, alkyl dimethoxypropionates, and alkyl diacetylglycerates. In all of these cases the effect on molecular rotation of alkylating the OH-group attached to an asymmetric carbon atom is much greater than that produced by acetylating the same group.

EXPERIMENTAL.

Menthoxyacetic Acid, $C_{10}H_{19}\cdot O\cdot CH_2\cdot CO_2H$.—Two hundred grams of menthol (Kahlbaum) were dissolved in about 500 c.c. of sodium-dried benzene in a 3-litre, round-bottom flask. Forty grams of

sodium cut up into thin plates were then added, and the flask was heated under a reflux condenser on a boiling-water bath for four hours. The excess of sodium was then removed (only 30 grams being required by 200 grams of menthol), and 50 grams of chloroacetic acid, dissolved in about 400 c.c. of dry benzene, were then added gradually, the flask being well shaken during the addition to keep the precipitated sodium chloroacetate in a finely divided state, and cooled when necessary to prevent violent boiling during the reaction. The result of this is to produce a gelatinous precipitate of sodium chloroacetate, on which the sodium menthoxide is able to react to form the sodium salt of menthoxyacetic acid. It is apparent that two molecules of sodium menthoxide must be present for every molecule of chloroacetic acid, as the reaction takes place in two stages:

(1) $CH_2Cl{\cdot}CO_2H + NaO{\cdot}C_{10}H_{19} = CH_2Cl{\cdot}CO_2Na + C_{10}H_{20}O$.

(2) $CH_2Cl{\cdot}CO_2Na + NaO{\cdot}C_{10}H_{19} = C_{10}H_{19}{\cdot}O{\cdot}CH_2{\cdot}CO_2Na + NaCl$.

In the actual preparation the quantities taken were in the proportion of $2\frac{1}{3}$ molecules of sodium menthoxide to 1 molecule of chloroacetic acid. At first sight it would seem to be more economical were the sodium chloroacetate prepared in some other way instead of utilising sodium menthoxide as in the first equation, but this is practically the only serviceable way, and the excess of menthol is easy to recover.

The flask was then heated under a reflux condenser for twenty-five hours on a boiling-water bath. During this time the pasty sediment was periodically broken up by vigorous shaking, and dry benzene to the extent of $1\frac{1}{2}$ litres added at intervals to keep the mixture in a sufficiently liquid condition.

The sodium menthoxyacetate was then washed out with water, which also dissolves the sodium chloride, sodium hydroxide, and any free chloroacetic acid. The menthol remains in the benzene layer, as well as any tarry products if formed. The aqueous solution of sodium menthoxyacetate was acidified with sulphuric acid, and the free menthoxyacetic acid extracted with ether. The extract after being dried was concentrated to a syrup, which crystallised out in the refrigerator. The crystals were washed free from mother liquor with a little ether, and dried on porcelain.

This product was almost colourless, and melted only 3° below that of the purified acid. The total yield of this crude acid was 85 grams, which is 75 per cent. of the theoretical quantity obtainable from the chloroacetic acid used.

The acid is very soluble in all organic solvents; it was purified by repeated recrystallisation from ether. After six such crystallisa-

[illegible] the melting point was 53—54°, and the rotation in methyl alcohol at 20° was:

l.	p.	D_4^{20}.	c.	α_D.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
[illegible]	5·253	0·8030	4·218	−7·84°	−92·93°	−198·8°

For the following preparations the acid was used after one crystallisation.

Menthoxyacetic Allylamide.—Ethyl menthoxyacetate was prepared by esterifying 60 grams of menthoxyacetic acid in an excess of absolute alcohol by saturation with dry hydrogen chloride. After heating for an hour, hydrogen chloride was again passed in, and the heating continued for another hour, after which the mixture was washed with a dilute solution of sodium carbonate, and the ester extracted with ether. After drying the extract, the ether was distilled over, and the ester distilled in a vacuum. The yield was [illegible] grams.

Fifteen grams of allylamine (Kahlbaum) were added, and the mixture heated under a reflux condenser on a water-bath for eight hours. The liquid product was purified by vacuum distillation until the observed rotation was constant. The yield was about 20 grams. After four distillations, the liquid boiled at 185—187°/14 mm., and gave $[\alpha]_D^{20}$ −76·11°.

The amide is a colourless, odourless, oily liquid, soluble in all organic solvents, but not in water or acids:

[illegible]·1466 gave 7·3 c.c. N_2 (moist) at 19° and 744·7 mm. N = 5·61.

$C_{15}H_{27}O_2N$ requires N = 5·53 per cent.

Densities:

t	20°.	30°.	50°	70°.	97°.
D_4^t	0·9667	0·9590	0·9442	0·9290	0·9082

Menthoxyacetic Allylamide.

Rotations in a 1-dcm. tube:

t.	D_4^t (from curve).	α_D^t.	$[\alpha]_D^t$.	$[M]_D^t$.
[illegible]	0·9667	−73·58°	−76·11°	−192·5°
[illegible]	0·9445	71·72	75·93	192·1
[illegible]	0·9376	70·97	75·70	191·5
[illegible]	0·9304	70·31	75·57	191·2
[illegible]	0·9070	68·20	75·19	190·2

Rotation in methyl alcohol solution. (Substance slightly impure through being kept a year.)

p.	c.	D_4^{20}.	α_D^{20} (l=2).	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
[illegible]·3759	1·887	0·7944	−3·03°	−80·27°	−203·1°
[illegible]·9299	3·132	0·7990	5·02	80·13	202·7
[illegible]·1802	5·772	0·8039	9·14	79·18	200·3

Menthoxyacetic Propylamide.—This was prepared in an identical manner to the allylamide from 45 grams of the ester and 12 grams of propylamine (Kahlbaum). After five distillations the observed rotation not being constant, and there being only 12 grams of the purest fraction, a second preparation of the amide was commenced, and after five vacuum distillations was added to the first preparation. When the whole had been distilled three more times, the observed rotation became constant. The yield from the two preparations was 20 grams.

This pure substance boiled at 188—189°/16 mm., and gave $[\alpha]_D^{20}$ −75·96°. It is a colourless, odourless, oily liquid, similar in properties to the allylamide:

0·1410 gave 7·0 c.c. N_2 (moist) at 17·5° and 748·6 mm. N = [illegible]

$C_{15}H_{29}O_2N$ requires N = 5·49 per cent.

Densities:

$t°$.	20°.	30°.	50°.	70°.	97°.
D_4^t.	0·9545	0·9469	0·9320	0·9174	0·8958

Menthoxyacetic Propylamide.

Rotations in a 1-dcm. tube:

$t°$.	D_4^t. (from curve).	α_D.	$[\alpha]_D^t$.	$[M]_D^t$.
20·0	0·9545	−72·51°	−75·97°	−193·7°
33·5	0·9445	71·60	75·80	193·3
60·0	0·9240	69·83	75·57	192·7
99·0	0·8940	67·09	75·04	191·4

Rotation in methyl alcohol solution. (Substance slightly impure through being kept a year.)

p.	c.	D_4^{20}.	α_D^{20} (l = 2).	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
2·3051	1·835	0·7960	−2·98°	−81·20°	−207·1°
4·5327	3·625	0·7997	5·88	81·11	206·6
6·0106	4·818	0·8016	7·79	80·84	206·1
7·3065	5·875	0·8041	9·44	80·34	204·9

Allyl Menthoxyacetate.—Sixty-five grams of menthoxyacetic acid (1 mol.) and 57 grams of allyl alcohol (3 mols.) were mixed in a flask and saturated with dry hydrogen chloride. After heating on a water-bath for a short time, more hydrogen chloride was passed in, and the mixture again heated for an hour. The mixture was then washed with a solution of sodium carbonate, and the ester and excess of allyl alcohol extracted with ether. This extract was dried and the ether and alcohol distilled off. The ester was then distilled in a vacuum until the observed rotation was constant at 15° in a 0·5-dcm. tube. After seven distillations the ester boiled at 152°/40 mm., and gave $[\alpha]_D^{15}$ −93·04°. The yield was 20 grams.

This ester is a colourless, odourless, oily liquid, soluble in all organic solvents:

0·2758 gave 0·7130 CO_2 and 0·2559 H_2O. C = 70·51; H = 10·31.

$C_{15}H_{26}O_3$ requires C = 70·87; H = 10·23 per cent.

Densities:

t°.	15°.	20°.	30°.	40°.	60°.	80°.	99°.
D_4^t	0·9726	0·9682	0·9610	0·9528	0·9384	0·9222	0·9094

Allyl Menthoxyacetate.

Rotations in a 0·5-dcm. tube:

t°.	D_4^t (from curve).	α_D.	$[\alpha]_D^t$.	$[M]_D^t$.
14	0·9720	−45·28°	−93·15°	−236·6°
25	0·9640	44·11	91·51	232·4
30	0·9605	43·66	90·91	230·9
33	0·9580	43·31	90·42	229·7
42	0·9515	42·45	89·23	226·6
85	0·9193	38·18	83·06	211·0

Rotation in methyl alcohol solution:

p.	D_4^t.	c.	l.	α_D.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
4·025	0·8003	3·221	2-dcm.	− 5·40°	−83·81°	−212·9°
8·912	0·8067	7·189	2-dcm.	12·06	83·87	213·0

Propyl Menthoxyacetate.—The propyl alcohol used had to be fractionated, as it boiled over a range of ten degrees, 93—103°. The fraction boiling at 96·5—97·5° was used for this preparation.

This ester was prepared in a similar manner to the above, excess of the alcohol to the extent of 3 molecules to 1 molecule of the menthoxyacetic acid being taken.

Seventy grams of the acid were esterified with 60 grams of propyl alcohol by means of dry hydrogen chloride, as for the above ester.

The crude ester, after seven distillations in a vacuum, had a constant rotatory power, $[\alpha]_D^{20}$ −91·46°, and boiled at 172°/26 mm. The yield was 19 grams.

The ester is a colourless, odourless, oily liquid, soluble in all organic solvents, but not in water:

0·2588 gave 0·6660 CO_2 and 0·2558 H_2O. C = 70·18; H = 10·98.

$C_{15}H_{28}O_3$ requires C = 70·31; H = 10·93 per cent.

Densities:

t°.	15°.	20°.	40°.	70°.	99°
D_4^t.	0·9577	0·9547	0·9381	0·9144	0·8901

Propyl Menthoxyacetate.

Rotations in a 0·5-dcm. tube:

$t°$.	D_4^t (from curve.)	α_D.	$[\alpha]_D^t$.	$[M]_D^t$.
8·0	0·9638	−44·78°	−92·92°	−237·[illegible]
20·0	0·9547	43·66	91·46	234·1
30·0	0·9461	42·71	90·30	231·2
53·0	0·9275	40·42	87·16	223·1
57·0	0·9240	40·15	86·91	222·5
89·5	0·8973	37·02	82·50	211·2

A 10·2 per cent. solution in methyl alcohol gave $[\alpha]_D^{20}$ −82·64

p.	D_4^t.	c.	l.	α_D.	$[\alpha]_D^{20}$.	$[M]_D^{20}$.
10·250	0·8057	8·258	2-dcm.	−13·65°	−82·64°	[illegible]

Menthyl Allylaminoacetate.—Forty grams of menthyl chloroacetate, prepared from menthol and chloroacetic acid by esterification with dry hydrogen chloride, were dissolved in 100 c.c. of sodium-dried ether, and 20 grams of allylamine were added. The mixture was heated under a reflux condenser for three hours on a water-bath. The interaction takes place readily, as after a few seconds crystals of allylamine hydrochloride were seen. It is necessary to take twice the quantity of amine required to replace the chlorine in the menthyl chloroacetate in order to combine with the hydrogen chloride split off.

The amine hydrochloride was quickly collected, and washed with a little dry ether. The weight—15 grams—showed that the reaction was complete. The ether and any excess of amine was distilled off, and the crude ester distilled in a vacuum until the observed rotation became constant. After four distillations the ester boiled at 155—157°/17 mm., and gave $[\alpha]_D^{20}$ −63·47°. The yield was 12 grams.

The ester is a colourless, odourless liquid, soluble in all organic solvents:

0·3552 gave 0·9206 CO_2 and 0·3374 H_2O. C = 70·70; H = [illegible]

0·2570 „ 12·9 c.c. N_2 (moist) at 20° and 739·4 mm. N = [illegible]

$C_{15}H_{27}O_2N$ requires C = 71·15; H = 10·67; N = 5·53 per cent.

Densities:

$t°$.	12°.	20°.	40°.	69°.	100°.
D_4^t	0·9565	0·9488	0·9347	0·9133	0·8903

Menthyl Allylaminoacetate.

Rotations in a 0·5-dcm. tube:

t.	D^t_4 (from curve).	a_D.	$[a]^t_D$.	$[M]^t_D$.
16·2	0·9518	−30·27°	−63·60°	−160·9°
20·5	0·9488	30·09	63·43	160·5
46·5	0·9295	29·49	63·45	160·5
48·5	0·9280	29·41	63·38	160·35
69·0	0·9133	28·76	62·98	159·3
99·8	0·8903	27·95	62·79	158·8

Rotations in methyl alcohol in a 2-dcm. tube at 20°:

D^t_4	p.	c.	a_D.	$[a]^{20}_D$.	$[M]^{20}_D$.
0·7945	1·5009	1·192	−1·70°	−71·28°	−180·33°
0·7979	3·0045	2·398	3·35	69·87	176·77
0·7993	4·1738	3·336	4·52	67·74	171·38

Menthyl Propylaminoacetate.—This was prepared in the same way as the above allylaminoacetic ester. Thirty-nine grams of menthyl chloroacetate were dissolved in 50 c.c. of dry ether, and heated with 20 grams of propylamine. After seven distillations in a vacuum the observed rotation was constant, the ester boiling at 159—161°/17 mm., and having $[a]^{20}_D$ −62·03°. The yield was 5 grams.

This ester is colourless and odourless, and is soluble in all organic solvents:

0·3698 gave 0·9464 CO_2 and 0·3832 H_2O. C = 69·80; H = 11·51.
0·2590 „ 12·8 c.c. N_2 (moist) at 21° and 742·4 mm. N = 5·47.
$C_{15}H_{29}O_2N$ requires C = 70·59; H = 11·37; N = 5·49 per cent.

Densities:

t.	12°.	20°.	40°.	69°.	100°.
D^t_4	0·9406	0·9330	0·9185	0·8976	0·8753

Menthyl Propylaminoacetate.

Rotations in a 0·5-dcm. tube:

t.	D^t_4 (from curve).	a_D.	$[a]^t_D$.	$[M]^t_D$.
14·5	0·9368	−29·14°	−62·21°	−158·6°
20·0	0·9330	28·96	62·08	158·3
38·0	0·9195	28·55	62·10	158·4
44·5	0·9152	28·40	62·06	158·3
58·0	0·9052	28·08	62·04	158·2
66·0	0·8995	27·86	61·95	158·0
99·0	0·8756	27·10	61·90	157·8

Rotations in methyl alcohol in a 2-dcm. tube at 20°:

D^{20}_4	p.	c.	α.	$[\alpha]^{20}_D$.	[M]...
0·7969	2·9900	2·383	− 3·32°	− 69·67°	[illegible]
0·7989	4·5608	3·644	5·04	69·16	[illegible]
0·8057	8·9275	7·193	9·87	68·61	[illegible]

CHEMICAL LABORATORIES, UNIVERSITY,
EDGBASTON, BIRMINGHAM.

CCLVII.—*The Constitution of Ergothioneine: a Betaine Related to Histidine.*

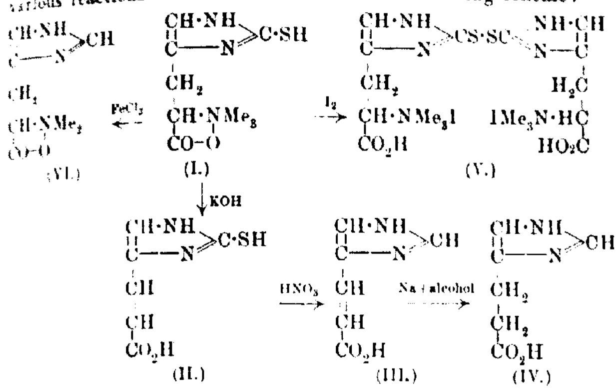
By GEORGE BARGER and ARTHUR JAMES EWINS.

Two years ago Tanret (*J. Pharm. Chim.*, 1909, [vi], **30**, 145) isolated from ergot a new crystalline base containing sulphur, and having the formula $C_9H_{15}O_2N_3S$. The description of the base given by Tanret suggested to us a possible relationship to the amino-acid histidine; thus ergothioneine, as the new base was called by Tanret, is precipitated by mercuric chloride, and forms a compound with silver. These properties, together with the large nitrogen content, were strongly suggestive of the presence of a glyoxaline ring. Since one of us in conjunction with H. H. Dale (Trans., 1910, **97**, [illegible]) had already isolated another histidine derivative from ergot, namely, 4(or 5)-β-aminoethylglyoxaline, a substance of great physiological activity and interest, we prepared a small quantity of ergothioneine according to Tanret's method, and found that, like histidine and many other glyoxaline derivatives, it gives an intense red coloration with sodium *p*-diazobenzenesulphonate, thus still further supporting our surmise with regard to the constitution of this base.

Ergothioneine contains (in addition to the sulphur atom) three carbon atoms and six hydrogen atoms more than histidine. These might well result from the substitution of three hydrogen atoms of histidine by methyl groups in such a manner that ergothioneine would be a new member of the class of methylated amino-acids or betaines, of which a number of examples are now known to occur in plants. This hypothesis proved to be correct; the substance is indeed a betaine, and almost certainly β-2-thiolglyoxaline-4(or 5)-propiobetaine (I). Like other betaines it has no marked physiological action.

On boiling with a concentrated (50 per cent.) aqueous solution of potassium hydroxide, the base is decomposed quantitatively into

trimethylamine and a yellow acid of the composition $C_6H_6O_2N_2S$, which represents the whole of the remaining atoms in the molecule, and the constitution of which is represented by (II). On boiling with dilute nitric acid, the sulphur atom of this acid is completely removed, and a new acid, β-glyoxaline-4(or 5)-acrylic acid (III), is formed. This acid on reduction yields β-glyoxaline-4(or 5)-propionic acid (IV), and we were able to identify both the saturated and the unsaturated acid by comparison with synthetic specimens. The various reactions will be best seen from the following scheme:



The only doubtful point remaining was with regard to the position of the sulphur atom. There are two probable positions, namely, attachment to the β-carbon atom of the side-chain or to the carbon atom in the 2-position in the glyoxaline ring, and choice between these two, although decisive, is based on analogy rather than on direct evidence; indeed, synthesis seems to be the only means of supplying complete proof.

The sulphur in ergothioneine reacts in every way like that of the thiolglyoxalines, and quite different from that in cystein, with which it might be expected to show analogies if attached to the β-carbon atom of the side-chain; thus the sulphur in cystein, as is well known, is readily eliminated by boiling with sodium hydroxide, whereas, as was stated above, the sulphur of ergothioneine is not removed by boiling with the strongest solutions of potassium hydroxide. On the other hand, the sulphur atom, like that of the thiolglyoxalines, is readily and quantitatively oxidised by ferric chloride (as recently employed by Pyman) or by bromine water to sulphuric acid, whereas in the case of cystein a sulphonic acid results, in which the sulphur still remains attached to the carbon atom. The only oxidising agent which acts similarly on cystein and ergo-

thioneine is iodine, which oxidises both to a compound, in which two sulphur atoms are directly linked. That obtained from ergothioneine has the constitution (V).* A further argument for considering ergothioneine to be a thiolglyoxaline derivative is the fact that, like other betaines, it is a feeble mono-acid base, whereas we should expect it to be di-acid if it, like histidine, contained a simple glyoxaline ring. The basic properties of the ring are destroyed by the presence of the sulphur atom as in other thiolglyoxalines (compare, for instance, 2-thiol-4(or 5)-aminomethylglyoxaline, which forms a mono-hydrochloride, and was recently described by Pyman, Trans., 1911, **99**, 672).†

Treatment of ergothioneine with ferric chloride gave trimethylhistidine (VI), a betaine which may possibly occur in nature.

Experimental.

The Action of Boiling 50 per cent. Aqueous Potassium Hydroxide on Ergothioneine.

0·88 Gram of ergothioneine was boiled with 20 c.c. of a 50 per cent. aqueous solution of potassium hydroxide, the distillate being collected in a known volume of *N*-hydrochloric acid. Distillation was continued until the evolution of alkaline vapours was practically complete. It was found that 3·1 c.c. of *N*-hydrochloric acid had been neutralised, corresponding with 80 per cent. of the theoretical for the evolution of one nitrogen atom. The main bulk of the distillate was evaporated to dryness, and the residue dissolved in a little alcohol and treated with an alcoholic solution of platinic chloride, when trimethylamine platinichloride (m. p. 241°) separated. (Found, Pt = 36·9. Calc., Pt = 36·9 per cent.)

One nitrogen atom was thus shown to be evolved as trimethylamine. The strongly alkaline residue in the flask was rendered acid to Congo-red, when there was at once precipitated as a yellow amorphous solid, *β-2-thiolglyoxaline-4-acrylic acid.*

This acid was found to be characterised by its general insolubility

* This iodide will be described later. It was already obtained by Tanret, who did not, however, appreciate its true significance. It forms black, steel grey or blue mixed crystals with iodine, a peculiar and extremely rare property which has so far only been observed in the case of cholalic acid, narceine, and saponarin, and is closely analogous to the adsorption of iodine by starch. For this reason Tanret, who analysed the compound, did not obtain results in agreement with any single formula.

† Dr. Pyman has since informed us of his recent observation that thiolglyoxalines are sharply differentiated from glyoxalines by the fact that they at once decolorise a dilute cold solution of potassium permanganate; we find that ergothioneine also does this, but histidine does not, nor does cystine.

is only moderately soluble in pyridine, and almost insoluble in all other ordinary organic solvents. The acid was crystallised for analysis by making a very dilute solution (0·1 per cent.) of the sodium salt, and acidifying. After three or four hours the acid began to separate, and precipitation was complete in about thirty-six hours. The acid obtained in this way separated in clusters of small prisms, which did not melt below 275°:

0·1179 gave 0·1805 CO_2 and 0·0420 H_2O. C=41·8; H=3·9.
$C_6H_6O_2N_2S$ requires C=42·3; H=3·5 per cent.

By oxidation by means of dilute nitric acid as described below, per cent. of the theoretical amount of sulphur was obtained from the filtrate as barium sulphate.

The Action of Boiling Dilute Nitric Acid on β-2-Thiolglyoxaline-4-acrylic Acid.

0·4 Gram of amorphous β-2-thiolglyoxaline-4-acrylic acid was added in small portions to 20 c.c. of 10 per cent. aqueous nitric acid. The mixture was kept gently boiling on a sand-bath for some minutes after solution was complete, and then allowed to cool. The crystalline *nitrate* of *β-glyoxaline-*4(or 5)*-acrylic acid* separated out, which after washing and drying melted at 198° with explosive decomposition. The yield was 0·28 gram:

0·1114 gave 0·1470 CO_2 and 0·0404 H_2O. C=36·0; H=4·0.
$C_6H_6O_2N_2,HNO_3$ requires C=35·8; H=3·5 per cent.

*β-Glyoxaline-*4(or 5)*-acrylic acid* was most readily obtained from the nitrate by the addition of one equivalent of sodium carbonate (solid) to a concentrated aqueous solution of the salt, when the acid separates at once as a crystalline solid, which after recrystallisation from dilute acetone was quite pure, and melted at 235—236°:

0·1776 gave 0·3474 CO_2 and 0·0712 H_2O. C=53·3; H=4·4.
$C_6H_6N_2O_2$ requires C=52·2; H=4·3 per cent.

β-Glyoxaline-4(or 5)-acrylic acid is moderately soluble in cold, but very readily so in hot, water. Its solutions give an intense red colour with sodium *p*-diazobenzenesulphonate.

The *phosphotungstate* is readily soluble in hot water or cold acetone, and crystallises in small, rectangular plates from dilute acetone.

The *picrate* forms golden-yellow prisms, melting at 213—214°, and sparingly soluble in cold water. The melting point of this picrate

remained unchanged when mixed with a synthetic specimen. The latter we obtained in small quantity by the action of trimethylamine on α-chloro-β-glyoxaline-4(or 5)-propionic acid.

The Reduction of β-Glyoxaline-4(or 5)*-acrylic Acid to β-Glyoxaline-4*(or 5)*-propionic Acid.*

β-Glyoxaline-4(or 5)-acrylic acid was dissolved in a little absolute alcohol, and the hot solution treated with five to six atomic proportions of sodium. The solution was then acidified with hydrochloric acid, and the precipitated salt collected. The filtrate and washings were evaporated to dryness, the residue dissolved in 5 per cent. aqueous sulphuric acid, and precipitated with phosphotungstic acid. The precipitate was treated with acetone, filtered from undissolved material, and the soluble phosphotungstate decomposed in the usual manner. On concentrating the final filtrate a crystalline acid separated, which after recrystallisation melted at 202°. When mixed with a specimen of synthetic β-glyoxaline-4(or 5)-propionic acid (m. p. 202°), the melting point remained unaltered. The acid obtained on reduction was therefore proved to be β-glyoxaline-4(or 5)-propionic acid.

The Action of Ferric Chloride on Ergothioneine. Formation of β-Glyoxaline-4(or 5)*-propiobetaine (Histidine-betaine).*

One gram of ergothioneine was boiled for one hour with an aqueous solution containing nine molecular proportions of ferric chloride. The iron was removed from solution by sodium carbonate, the filtrate acidified with sulphuric acid (so as to give a 5 per cent. solution of the latter), and precipitated by phosphotungstic acid. The precipitate, which was completely soluble in acetone, was decomposed in the usual way, and the barium and sulphuric acid removed. The filtrate was concentrated, and treated with a hot aqueous solution of picric acid. On cooling, a crystalline picrate separated, which after recrystallisation from water was obtained in deep yellow prisms melting at 123°:

0·1340 gave 0·1908 CO_2 and 0·0396 H_2O. C = 38·4; H = 3·3.

$C_9H_{15}O_2N_3(C_6H_3O_7N_3)_2$ requires C = 38·5; H = 3·3 per cent.

The *dipicrate* is very sparingly soluble in cold, fairly readily so in hot, water.

The *picrolonate* prepared in the usual way forms long, thin, orange-yellow needles, melting at 229—230°.

The *aurichloride* separated from dilute aqueous hydrochloric acid as large, broad, deep orange-yellow prisms, melting at 171°.

In conclusion, we wish to express our indebtedness to Dr. F. L. Pyman for synthetic specimens of α-chloro-β-glyoxaline-4(or 5)-propionic and β-glyoxaline-4(or 5)-propionic acids for purposes of comparison, and to the Wellcome Chemical Works, Dartford, for a supply of ergothioneine.

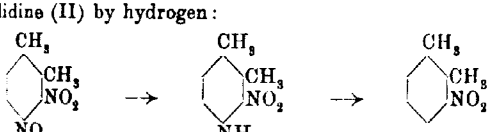
THE WELLCOME PHYSIOLOGICAL RESEARCH LABORATORIES,
BROCKWELL HALL, HERNE HILL, LONDON, S.E.

CLVIII.—*Derivatives of* o-*Xylene. Part I.* 3-*Nitro*-o-*xylene and* 3 : 6-*Dinitro*-o-*xylene.*

By ARTHUR WILLIAM CROSSLEY and GERTRUDE HOLLAND WREN.

IN 1909 an account of the preparation and properties of 3-nitro-o-xylene was published (Trans., **95**, 208). The method adopted for its isolation (*ibid.*, p. 216) consisted in treating *o*-xylene with a mixture of nitric and sulphuric acids and separating the two mono-nitro-*o*-xylenes from the dinitro-*o*-xylenes by distillation. The mixture of 3- and 4-nitro-*o*-xylenes was then distilled fractionally, and each fraction cooled, when 4-nitro-*o*-xylene separated as a yellow solid, melting at 30°. After repeating this process several times, the residual liquid product was refractioned, when finally an oil, boiling at 131°/20 mm., was obtained, which was proved to be 3-nitro-*o*-xylene by the fact that it gave on oxidation an almost quantitative yield of 3-nitrophthalic acid. Nevertheless, the method of preparation is not without objection, for despite the numerous fractional distillations carried out, it is possible that the resulting 3-nitro-*o*-xylene might contain a small quantity of 4-nitro-*o*-xylene dissolved in it, and it seemed of interest to prepare 3-nitro-*o*-xylene by some other method, in which the isomeric 4-nitro-*o*-xylene would not be produced, and to compare the physical constants of the two specimens of 3-nitro-*o*-xylene.

The method adopted was to replace the amino-group in 3-nitro-*o*-4-xylidine (II) by hydrogen:



(I.) (II.) (III.)

3-Nitro-*o*-4-xylidine (II) has been described by Noelting, Braun, and Thesmar (*Ber.*, 1901, **34**, 2249), and that these authors orien-

tated this compound correctly receives confirmation from the experiments now described. They prepared it by the action of a mixture of nitric and sulphuric acids on *o*-4-xylidine. The same substance may be more easily obtained by reducing 3:4-dinitro-*o*-xylene (I) with alcoholic stannous chloride, for which purpose 10 grams of 3:4-dinitro-*o*-xylene (Trans., 1909, **95**, 210) were suspended in 75 c.c. of absolute alcohol, and a solution of 40 grams of stannous chloride in 200 c.c. of absolute alcohol, saturated with dry hydrogen chloride, gradually added, the temperature being maintained between 10° and 12°. After remaining twenty-four hours the major portion of the alcohol was evaporated, and the residue poured into water, when on some occasions it was found necessary to filter from a small amount of unchanged dinitroxylene. Solid potassium hydroxide was then added until the precipitate originally formed, redissolved, when the nitroamine separated. This was extracted with ether, etc., when the residue, weighing 7·5 grams, solidified. It was purified by crystallisation from dilute alcohol, yielding 4·6 grams of 3-nitro-*o*-4-xylidine (compare Noelting, Braun, and Thesmar, *loc. cit.*) as scarlet-coloured needles, melting at 65—66°. On evaporating the alcoholic mother liquor and submitting the residue to steam distillation, a further 1·3 grams of pure nitroamine were isolated, thus making the total yield 75 per cent. of that theoretically capable of being formed from the dinitroxylene employed. Although indications of the presence of the isomeric 4-nitro-*o*-3-xylidine were obtained, this substance has not, so far, been isolated in a pure condition.

3-Nitro-o-xylene from 3-Nitro-o-4-xylidine.

Two quantities of 5 grams of pure 3-nitro-*o*-4-xylidine were powdered and separately dissolved in a mixture of 30 c.c. of concentrated sulphuric acid and 5 c.c. of water, cooled in ice, and a solution of 2·1 grams of sodium nitrite in 10 c.c. of water gradually added, the temperature not being allowed to rise above 5°. The whole was then poured into 200 c.c. of boiling ethyl alcohol, heated for half an hour, the major portion of the alcohol evaporated, and the residue distilled in a current of steam, when an oil passed over readily. It was extracted with ether, washed with sodium hydroxide solution, then with water, dried over calcium chloride, and the ether evaporated, when 7 grams (theory, 9 grams) of liquid were obtained, boiling constantly at 13[illegible]° 29 mm.:

0·2017 gave 15·8 c.c. N_2 (moist) at 17° and 762 mm. N = 9·11.

$C_8H_9O_2N$ requires N = 9·27 per cent.

3-Nitro-o-xylene is a clear, pale yellow, refractive liquid boiling at 240°/760 mm., solidifying on cooling, and melting sharply at 15°. When dissolved in alcohol and the solution cooled in ice, it crystallises readily in radiating clusters of almost colourless, transparent needles.

A comparison of the properties of pure 3-nitro-*o*-xylene with those of the substance previously described is given in the following table, from which it is evident that the latter was not quite pure, although, considering its method of preparation, its comparative purity is rather remarkable.

	Source.	B. p.	B. p.	M. p.
3-Nitro-*o*-xylene	Xylene + HNO_3 + H_2SO_4	245—246°/760 mm.	131°/20 mm.	7—9°
3-Nitro-*o*-xylene	3 : 4-Dinitro-*o*-xylene	240°/760 mm.	136°/29 mm.	15°

In order to obtain some idea of the amount of 4-nitro-*o*-xylene contained in the 3-nitro-*o*-xylene prepared by the action of a mixture of nitric and sulphuric acids on *o*-xylene, the melting points of mixtures of 3-nitro-*o*-xylene with definite amounts of 4-nitro-*o*-xylene were determined.

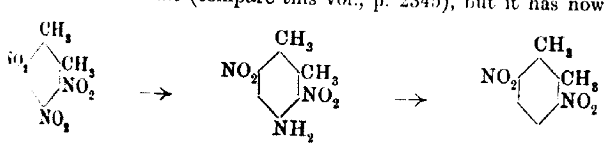
		Melting point.
3-Nitro-*o*-xylene, *pure*		15°
,,	+ 1 per cent. of 4-nitro-*o*-xylene	12—14°
,,	+ 2 ,, ,,	11·5—13·5°
,,	+ 5 ,, ,,	9—11°
,,	+ 10 ,, ,,	5—8°

From these figures it would appear that the 3-nitro-*o*-xylene prepared from *o*-xylene by the action of nitric and sulphuric acids contains about 7 per cent. of 4-nitro-*o*-xylene.

3 : 6-*Dinitro-o-xylene*.

The preparation of 3 : 6-dinitro-*o*-xylene by the nitration of 3-nitro-*o*-xylene has been described (Trans., 1909, **95**, 210), but as the substance was produced in such minute quantities the properties ascribed to it were given with some reserve. Experiments with much larger quantities of material have now been carried out, and the substance has been obtained pure.

Attempts to prepare 3 : 6-dinitro-*o*-xylene by the elimination of the nitro-group in position 4 from 3 : 4 : 6-trinitro-*o*-xylene did not give the desired result (compare this vol., p. 2345), but it has now



been isolated in a pure condition by further nitrating 3-nitro-*o*-xylene, and also from the residues obtained in the preparation of 3:4-dinitro-*o*-xylene (*ibid.*, p. 216), which residues contain about 0·3 to 0·5 per cent. of 3:6-dinitro-*o*-xylene.

Nitration of 3-Nitro-o-xylene.—Sixty grams of 3-nitro-*o*-xylene were nitrated and worked up as already described (Trans., [illegible], **95**, 214) to give the substance of a waxy nature, melting at [illegible] (1·1 grams), previously stated to be 3:6-dinitro-*o*-xylene. On further crystallisation from alcohol it gave a small amount of a substance melting sharply at 89—90°, which, as shown later, is the true melting point of 3:6-dinitro-*o*-xylene.

Nitration of o-Xylene.—It has been shown (*ibid.*, p. 216) that when *o*-xylene is nitrated with fuming nitric acid, there are produced 3:4-dinitro-*o*-xylene, 4:6-dinitro-*o*-xylene, a mixture of 4:5-dinitro-*o*-xylene and 3:4-dinitro-*o*-xylene of constant melting point, and a waxy solid of low melting point. It was thought from its nature that the latter substance would contain 3:6-dinitro-*o*-xylene, and such has been proved to be the case. To isolate it, 1250 grams of *o*-xylene were nitrated in quantities of 25 grams at one time, and the resulting solid worked up (*ibid.*, p. 21[illegible]) for the separation of the dinitro-*o*-xylenes by alternate treatment with sulphuric acid and then alcohol, involving between five hundred and six hundred crystallisations from either sulphuric acid or alcohol. In this manner nearly 300 grams of the waxy solid of low melting point were obtained, which in quantities of 20 grams at one time were again submitted to fractional crystallisation from sulphuric acid and then alcohol (two hundred crystallisations), when 65 grams were obtained, melting at 50—60°. This latter substance was finally fractionated (one hundred crystallisations) from alcohol, when 3 grams of solid were obtained, melting sharply at 89—90°.

0·1355 gave 16·8 c.c. N_2 (moist) at 758 mm. and 20°. N = 14·[illegible].

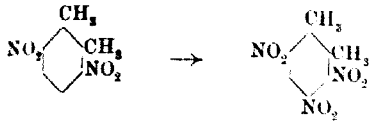
$C_8H_8O_4N_2$ requires N = 14·29 per cent.

3:6-*Dinitro-o-xylene* is very soluble in the cold in the ordinary organic solvents, except alcohol, from which it crystallises in sheaves of small needles melting at 89—90°. It is not identical with any of the other three dinitro-*o*-xylenes, as proved by the following mixed melting-point determinations:

	M. p.		M. p.	Mixed m. p.
3 : 6-Dinitro-*o*-xylene	89—90°	3 : 4-Dinitro-*o*-xylene	82°	59—[illegible]
,,	89—90	3 : 5-Dinitro-*o*-xylene	75	45—52
,,	89—90	4 : 5-Dinitro-*o*-xylene	115	60—[illegible]

3:6-Dinitro-*o*-xylene should on further nitration yield only 3:4:6-trinitro-*o*-xylene, and not the isomeric 3:4:5-trinitro-*o*-xylene. In order to prove this point, 1 gram of pure 3:6-dinitro-

xylene was further nitrated by treatment with fuming nitric acid, when 1·2 grams (theory, 1·22 grams) of trinitro-o-xylene were



obtained, which after crystallisation from alcohol melted at 72°, nor was any trace of the isomeric trinitro-o-xylene, melting at 115°, detected, although, as already shown, the separation of the two isomeric trinitro-o-xylenes is a very simple process.

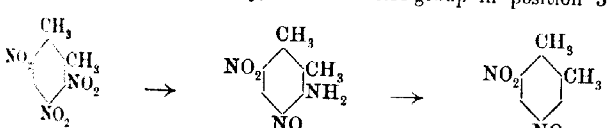
Research Laboratories, Pharmaceutical Society,
17, Bloomsbury Square, W.C.

CLIX.—*Derivatives of* o-*Xylene. Part II. Dinitro*-o-*xylidines.*

By Arthur William Crossley and George Francis Morrell.

The experiments described in this communication originated with the desire to find a method for preparing 3:6-dinitro-o-xylene which would be less tedious and give larger yields than that described on p. 2343 of this volume.

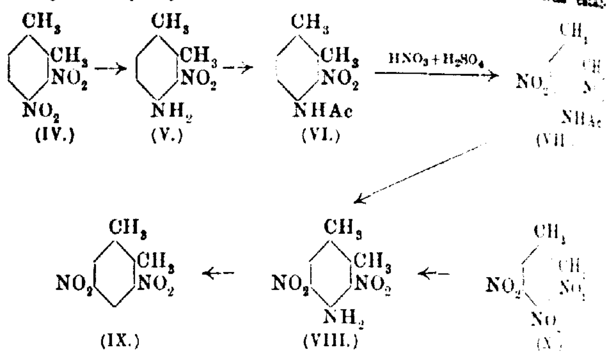
In the first place, the action of reducing agents on 3:4:6-trinitro-o-xylene (I) was tried in the hope that it might be found possible to convert the nitro-group in position 4 into an amino-group, which could then be replaced by a hydrogen atom. Reduction with ammonium sulphide gave rise entirely to sulphur compounds, which were not further examined, and stannous chloride gave equally unsatisfactory results. Alcoholic ammonia, however, reduced 3:4:6-trinitro-o-xylene readily, but the nitro-group in position 3



(I.) (II.) (III.)

was the one to be attacked, and there resulted 4:6-dinitro-o-3-xylidine (II), which is proved by the fact that when the dinitroamine is diazotised and the diazo-group replaced by a hydrogen atom, 4:6-(3:5)-dinitro-o-xylene (III) is produced. The nitro-o-xylenes mentioned in this communication were described in the Transactions, 1909, **95**, 202.

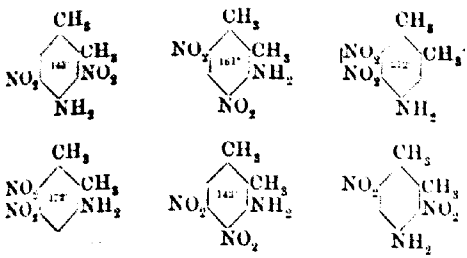
The next attempt consisted in nitrating 3-nitroaceto-o-4-xylidide (VI), which was prepared by acetylating 3-nitro-o-4-xylidine (V), obtained by the reduction of 3:4-dinitro-o-xylene (IV) with stannous chloride, but the nitro-group, instead of entering position 6, as was thought possible, takes up position 5, giving 3:5-dinitroaceto-o-4-xylidide (VII). The constitution of this substance was established



(IV.) (V.) (VI.) (VII.) (IX.) (VIII.) (X.)

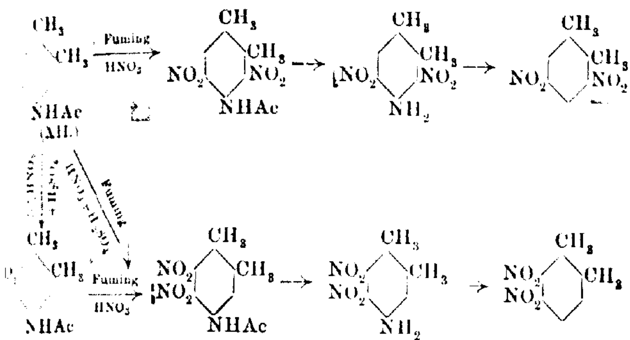
lished by removal of the acetylamino-group, when 3:5-dinitro-o-xylene (IX) is obtained. 3:5-Dinitro-o-4-xylidine is also produced by the reduction of 3:4:5-trinitro-o-xylene (X) with alcoholic ammonia.

Having proceeded so far, it seemed of interest to attempt the preparation of all the six possible dinitro-o-xylidines which on theoretical grounds should exist. Five of them are now described, the missing 3:6-dinitro-o-4-xylidine (XI) being the one which it was desired to prepare for the initial object of this research. In the reactions which have been tried, wherever it was possible for two different dinitroamines to result, evidence was forthcoming to show that both isomerides were formed, although one of the two was always obtained in largely predominating amount. It is therefore quite possible that 3:6-dinitro-o-4-xylidine is produced in some of these reactions, but under the conditions tried the amount must have been extremely small, and its isolation for all practical purposes an impossibility.



(XI.)

The next series of reactions consisted in nitrating aceto-o-4-xylidide (XII) under varying conditions, and the results are readily followed on consulting the accompanying diagram:

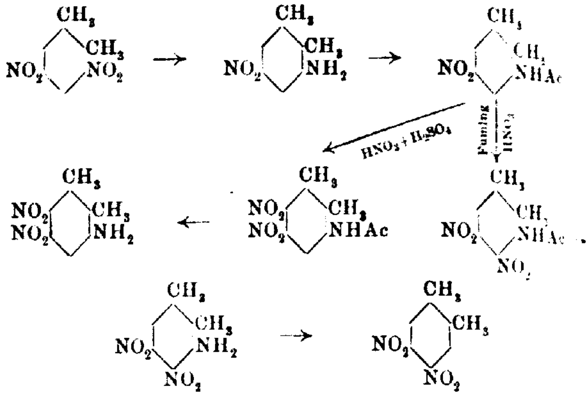


The product with fuming nitric acid alone, after elimination of the acetyl group, is identical with the substance obtained by the action of alcoholic ammonia on 3:4:5-trinitro-o-xylene, and is therefore 3:5-dinitro-o-4-xylidine.

A mixture of nitric and sulphuric acids gives a new dinitroamine, in which the position of the nitro-groups was ascertained by elimination of the amino-group, when 5:6-(3:4)-dinitro-o-xylene resulted. The dinitroamine is therefore 5:6-dinitro-o-4-xylidine, which can also be prepared from aceto-o-4-xylidide by first treating it with a mixture of 70 per cent. nitric acid and sulphuric acid, and nitrating the resulting 6-nitroaceto-o-4-xylidide with fuming nitric acid (compare Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2251).

Two other dinitro-o-xylidines were obtained by nitrating 5-nitro-

aceto-*o*-3-xylidide, involving the series of reactions indicated by the following formulæ:



With fuming nitric acid 4:5-dinitro-*o*-3-xylidine is formed, as proved by the fact that removal of the amino-group gives rise to 4:5-dinitro-*o*-xylene, whereas 5:6-dinitro-*o*-3-xylidine results from the action of a mixture of nitric and sulphuric acids. This dinitro-amine was not converted into a dinitro-*o*-xylene, for as only two dinitro-*o*-xylidines can result from the nitration of 5-nitroaceto-3-*o*-xylidide and the constitution of one of the two has been decided, no doubt can exist as to the position of the nitro-groups in the second product of nitration.

Experimental.

Reduction of 3:4:6-*Trinitro-o-xylene.*

3:4:6-Trinitro-*o*-xylene in quantities of 10 grams at one time was suspended in 100 grams of absolute alcohol, and dry ammonia passed in until the solution was saturated. The liquid first turned blue, then deep purple, changing to deep red as the trinitro-*o*-xylene passed into solution. The whole was allowed to remain for twenty-four hours, when a bronze-green, crystalline solid (7 grams) had separated. This was collected, and extracted with boiling alcohol, when 5·2 grams of fine, yellow needles were obtained. The insoluble residue was not further examined:

0·1909 gave 0·3208 CO_2 and 0·0720 H_2O. C=45·73; H=4·19.

0·1188 „ 20·3 c.c. N_2 (moist) at 20° and 757 mm. N=19·6.

$C_8H_9O_4N_3$ requires C=45·50; H=4·26; N=19·90 per cent.

4:6-*Dinitro-o-3-xylidine* is readily soluble in cold acetone or on warming in ethyl acetate, chloroform, or benzene, and crystallises from alcohol in fine, golden-yellow needles, melting at 161°.

The *diacetyl* derivative, prepared by heating the amine with a mixture of equal parts of acetyl chloride and acetic anhydride on the water-bath for three hours, is readily soluble in the cold in chloroform, readily on warming in benzene, ethyl acetate, or acetone, and crystallises from alcohol in large, transparent, fern-like aggregates, melting at 139°:

0·1741 gave 21·2 c.c. N_2 (moist) at 15° and 758 mm. N = 14·22.

$C_{12}H_{13}O_6N_3$ requires N = 14·24 per cent.

To determine the number of acetyl groups, the substance was hydrolysed with alcoholic potassium hydroxide, the alcohol evaporated, the residue acidified with sulphuric acid, distilled in a current of steam, and the acetic acid titrated with *N*/10-sodium hydroxide solution:

0·5413 required 0·232 gram NaOH. $CH_3·CO$ = 29·6.

$C_8H_7O_4N_3(CH_3·CO)_2$ requires $CH_3·CO$ = 29·1 per cent.

Conversion of 4:6-*Dinitro*-o-3-*xylidine into* 4:6-*Dinitro*-o-*xylene*.

Four grams of 4:6-dinitro-*o*-3-xylidine were dissolved in a mixture of 24 c.c. of concentrated sulphuric acid and 4 c.c. of water, the whole cooled in a freezing mixture, and the calculated quantity of 10 per cent. solution of sodium nitrite gradually added (compare Blanksma, *Rec. trav. chim.*, 1909, **28**, 93). The whole was then poured into 100 c.c. of boiling ethyl alcohol, heated for thirty minutes, poured into water, and the precipitated solid crystallised from alcohol, when it melted at 75°; nor was this melting point lowered on mixing with pure 4:6-dinitro-*o*-xylene:

0·1011 gave 12·6 c.c. N_2 (moist) at 18° and 761 mm. N = 14·40.

$C_8H_8O_4N_2$ requires N = 14·29 per cent.

Reduction of 3:4:5-*Trinitro*-o-*xylene*.

Ten grams of 3:4:5-trinitro-*o*-xylene were reduced with alcoholic ammonia as described in the case of the isomeric trinitroxylene (p. 2348), when 8·8 grams of crude material were obtained. No part of the reduction product was insoluble in alcohol:

0·1100 gave 18·8 c.c. N_2 (moist) at 20° and 768 mm. N = 19·76.

$C_8H_9O_4N_3$ requires N = 19·9 per cent.

3:5-*Dinitro-o-4-xylidine* is readily soluble in the cold in chloroform, benzene, or ethyl acetate, and crystallises from ethyl alcohol in orange-red needles, melting at 143°.

The *acetyl* derivative, prepared by heating the nitroamine with a mixture of equal parts of acetic anhydride and acetic acid, crystallises from alcohol in transparent needles, melting at 223°.

0·1204 gave 16·8 c.c. N_2 (moist) at 19° and 768 mm. N = 16·[illegible].

$C_{10}H_{11}O_5N_3$ requires N = 16·6 per cent.

The conversion of 3:5-dinitro-*o*-4-xylidine into 3:5-dinitro-*o*-xylene was carried out exactly as described in the case of 4:6-dinitro-*o*-3-xylidine (see p. 2349). The resulting substance crystallised from alcohol in needles, melting at 75°, nor was this melting point altered on admixture with pure 3:5-dinitro-*o*-xylene.

Nitration of 3-Nitroaceto-o-4-xylidide.

3-Nitroaceto-*o*-4-xylidide was prepared by reducing 3:4-dinitro-*o*-xylene with stannous chloride (compare this vol., p. 2342), and heating 2 grams of the resulting 3-nitro-*o*-4-xylidine with acetyl chloride for two hours. If the heating with acetyl chloride is continued for a longer period, a product of higher melting point, probably a diacetyl derivative, is produced. The excess of acetyl chloride was then evaporated, and the resulting viscid solid triturated with cold ethyl alcohol, when 2 grams of a clear, white solid were obtained, which crystallised from alcohol in stout, transparent needles, melting at 115° (compare Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2251).

One gram of 3-nitroaceto-*o*-4-xylidide was dissolved in 5 c.c. of concentrated sulphuric acid, cooled in a freezing mixture, and 15 c.c. of a mixture of one part of nitric acid (D 1·42) and two parts of concentrated sulphuric acid added, so that the temperature remained below −3°. The whole was allowed to remain at this temperature for two hours, poured on ice, filtered, the residue washed with a little ether, and crystallised from alcohol, when 9·4 grams of pure 3:5-dinitroaceto-*o*-4-xylidide were obtained.

The nitration was also carried out with fuming nitric acid and sulphuric acid, and also with nitric acid (D 1·5 and 1·42) alone; the former gave rise to the same dinitroaceto-*o*-xylidide, but in smaller yield, and with nitric acid only resinous products were obtained.

Nitration of Aceto-o-4-xylidide.

(*a*) *With Fuming Nitric Acid.*—One gram of aceto-*o*-4-xylidide was gradually added to 10 c.c. of fuming nitric acid, the temperature being maintained below −5°. The whole was poured on ice

and the precipitated solid (1·1 grams) crystallised from alcohol, when pure 3:5-dinitroaceto-*o*-4-xylidide, melting at 223°, was obtained.

(*b*) *With Fuming Nitric Acid and Sulphuric Acid.*—Five grams of aceto-*o*-4-xylidide were dissolved in 30 c.c. of concentrated sulphuric acid, cooled in a freezing mixture, and 45 c.c. of a mixture of one volume of nitric acid (D 1·5) and two volumes of sulphuric acid gradually added. The whole was poured on ice, the solid collected and crystallised from alcohol, when 5·1 grams of a substance melting at 170—171° were obtained:

0·1030 gave 14·8 c.c. N_2 (moist) at 20° and 754 mm. N = 16·30.

$C_{10}H_{11}O_5N_3$ requires N = 16·60 per cent.

5:6(3:4)-*Dinitroaceto*-o-4-*xylidide* crystallises from alcohol in fine, white needles melting at 173°. It was saponified by heating to 100° with ten times its weight of concentrated sulphuric acid for ten minutes, poured on ice, and the precipitate crystallised from alcohol:

0·1036 gave 18·2 c.c. N_2 (moist) at 22° and 753 mm. N = 19·72.

$C_8H_9O_4N_3$ requires N = 19·9 per cent.

5:6(3:4)-*Dinitro*-o-4-*xylidine* is only very moderately soluble in ethyl alcohol, benzene, or chloroform, and crystallises from acetone in deep orange-red needles, melting at 212°. When the amino-group was removed from this dinitroamine by the process described on p. 2349, it gave 3:4-dinitro-*o*-xylene, melting at 82°.

(*c*) *With Nitric Acid* (D 1·42) *and Sulphuric Acid.*—When aceto-4-xylidide was nitrated by adding to its solution in concentrated sulphuric acid a mixture of nitric acid (D 1·42) and concentrated sulphuric acid, it gave 6(3)-nitroaceto-*o*-4-xylidide, melting at 210°, and previously described by Noelting. The latter substance on treatment with fuming nitric acid was converted in good yield into 5:6(3:4)-dinitroaceto-*o*-4-xylidide, melting at 173°.

Nitration of 5-Nitroaceto-o-3-xylidide.

(*a*) *With Fuming Nitric Acid.*—5-Nitro-*o*-3-xylidine (m. p. 111°) was prepared by reducing 3:5-dinitro-*o*-xylene with stannous chloride (compare this vol., p. 2342). The acetyl derivative melting at 230° (compare Noelting, Braun, and Thesmar, *Ber.*, 1901, **34**, 2247) is best prepared by dissolving the amine in five times its weight of benzene, adding a solution of acetic anhydride (in amount equal to that of the amine taken) in benzene, warming for a minute or two, when the whole becomes semi-solid, and crystallising the solid from alcohol. Twenty-four c.c. of fuming nitric acid were gradually added to 2 grams of 5-nitroaceto-*o*-3-xylidide surrounded by a freezing mixture, the whole allowed to remain for one and

a-half to two hours at 8—10°, poured into ice-water, the precipitate washed with a little ether, and crystallised from alcohol:

0·1048 gave 15·2 c.c. N_2 (moist) at 22° and 767 mm. N = 16·[illegible]

$C_{10}H_{11}O_5N_3$ requires N = 16·6 per cent.

4:5-*Dinitroaceto-o-3-xylidide* is very readily soluble in acetone and ethyl acetate, moderately so in hot alcohol or benzene, and crystallises from alcohol in colourless needles, melting at 225°. It was hydrolysed by heating to 90° for five minutes with ten times its weight of concentrated sulphuric acid, poured into water, and the precipitate crystallised from alcohol:

0·1010 gave 17·3 c.c. N_2 (moist) at 20° and 769 mm. N = 19·[illegible]

$C_8H_9O_4N_3$ requires N = 19·9 per cent.

4:5-*Dinitro-o-3-xylidine* is readily soluble in the cold in acetone or ethyl acetate, readily so on warming in benzene or chloroform, and crystallises from alcohol in radiating clusters of orange needles, melting at 143°. On removal of the amino-group by the method already indicated, 4:5-dinitro-o-xylene, melting at 115°, is obtained.

(*b*) *With Fuming Nitric Acid and Sulphuric Acid.*—Six grams of 5-nitroaceto-o-3-xylidide were dissolved in 30 c.c. of concentrated sulphuric acid, and 90 c.c. of a mixture of one volume of fuming nitric acid and two volumes of sulphuric acid gradually added, allowed to remain at 8—10° for two hours, poured on ice, and the precipitate crystallised from a mixture of four parts of benzene and one part of acetone:

0·1012 gave 14·8 c.c. N_2 (moist) at 24° and 758 mm. N = 16·[illegible]

$C_{10}H_{11}O_5N_3$ requires N = 16·6 per cent.

5:6-*Dinitroaceto-o-3-xylidide* is readily soluble in alcohol, acetone, or ethyl acetate, and crystallises from the above-mentioned mixture of solvents in white plates, melting at 180°. It was hydrolysed by heating with ten times its weight of concentrated sulphuric acid for twenty minutes at 110—115°, and the product crystallised from alcohol and analysed:

0·1114 gave 19·7 c.c. N_2 (moist) at 24° and 756 mm. N = 19·71

$C_8H_9O_4N_3$ requires N = 19·90 per cent.

5:6-*Dinitro-o-3-xylidine* is readily soluble in the cold in ethyl acetate or acetone, and crystallises from alcohol in deep yellow needles, melting at 172°. It is soluble in concentrated hydrochloric acid to form a colourless solution, which deposits tabular crystals of a very unstable hydrochloride. This is the only dinitro-o-xylidine described in this communication which shows any tendency to form salts.

RESEARCH LABORATORY, PHARMACEUTICAL SOCIETY,
17, BLOOMSBURY SQUARE, W.C.

BERTHELOT MEMORIAL LECTURE.

DELIVERED ON NOVEMBER 23RD, 1911.

By HAROLD BAILY DIXON, M.A., Ph.D., F.R.S., Past-President of the Chemical Society.

(1) *His Career.*

In this age of extreme specialisation, the life and work of Berthelot teach the world the much-needed lesson that men of science are not necessarily men of one idea, but may be great, not only as experimenters, but great also as thinkers and as citizens. On all that he turned his mind to—and few things were foreign to his interest—Berthelot brought to bear, not only an exact scientific method and an exquisite clearness of statement, but an imagination as foreseeing as it was comprehensive, a patriotism as pure as it was enlightened. In the work of his life—whether as a philosopher or as a Cabinet Minister—Berthelot looked to Science as his guide. He believed in science as an illuminating and humanising force; he believed that in science lay the secret of the progress of France and of mankind. To pursue science was to ensure progress; science was to him a mission, a recreation, a religion. "To the end of my life," he wrote half-sadly to Renan (in 1892), "I shall be the dupe of this desire for progress which you so wisely relegate to the sphere of illusions." But of the reality of the progress achieved by Berthelot no chemist can doubt. In the realm of industry alone what tempting offers were made to him for a monopoly of his synthetic processes in organic chemistry. But Berthelot never bargained with or patented his discoveries. "The man of science," he declared, "should make the possession of Truth his only riches." Not that Berthelot considered the applications of science beneath him: on the contrary, he believed that science should be pursued largely by reason of its service to mankind. "Science has a double aim," he wrote, "an ideal aim which is the search for pure truth, and a positive and human aim which is the good of man and the development of civilisation."

Pierre Eugène Marcelin Berthelot * was born in the heart of the old Paris, in the Place de Grève—now Haussmannised out of recognition into the Place de l'Hôtel de Ville—on October 25th, 1827.

* I am indebted to the kindness of Berthelot's son—Prof. Daniel Berthelot—for these names and dates, and also for much other valuable information. I desire also to express my obligation to my old student, Mr. A. S. Robinson, for making me a précis of Berthelot's papers.

He died in Paris, March 18th, 1907. As he was born and bred so he lived and died a Parisian.

Through his father, Dr. Jacques Martin Berthelot, the son inherited his scrupulous regard for duty, his serious love for science, his liberal instincts, and his philosophic outlook on life; through his mother, Ernestine Sophie Claudine Béard, he inherited his ardent and responsive nature, his amazing industry, his versatility, and his curiosity. From the Place de Grève his family moved to a house near by in the narrow Rue des Ecrivains, just opposite the Tour Sainte-Jacques. The somewhat delicate and highly strung boy grew up in sight of those royal ceremonials—the Corpus Christi processions from the Tuileries to Notre Dame—when people in the street were obliged to kneel, under penalty of sacrilege, as the procession passed. As a child the roar of the revolution may have sounded in his ears, for his father's house overlooked the scene of many of those deeds of violence that marked the popular upheaval against the Ordinances of the 25th of July (1830). Then, as again in the later revolutions, the house became a hospital equally for Royalist and for Republican, for Dr. Berthelot made no distinction between his patients, however much his sympathy went out to the suffering people.

Even from the age of ten, Berthelot tells us, he began to ponder on the problems of life, and was troubled by the insecurity of the future. Nevertheless, he was an industrious and brilliant scholar, and made rapid progress at the school he attended—the Collège Henri IV. Sixty years later at the Jubilee Celebration, M. Fouqué, the President of the Académie des Sciences, bore striking testimony to Berthelot's gifts as a boy. "Everyone admires in you your power of work, your spirit of invention, your logic of ideas, your grasp of memory, your skill in experiment. . . . I affirm that these precious gifts you already possessed in the germ when you were still a simple schoolboy. More than half a century ago we sat side by side on the benches of the mathematical class in the Collège Henri IV.; a close comradeship grew up between us. My recollections bring back with pleasure the long talks we had on every kind of question. . . . I still see myself in discussion with you on the muddy road that led to your house at the foot of the Tower of Saint-Jacques. There I met the kindest greeting from your father, and then we climbed to your attic and resumed our interrupted argument—our only distraction being the swallows that built among the sculptures of the old tower."

At the end of his school course in 1846 he took the highest prize in competition with all the best students from the lycées of Paris

the "prix d'honneur de philosophie." To his sound classical education he attached great value, and his love of ancient literature lasted through life. Two old editions of Lucretius and of Tacitus, preserved from his schooldays, were his constant companions whenever he left Paris. He quoted Horace familiarly, and he has told us that he soon recovered his Greek when he began to decipher the Alexandrine MSS. on Alchemy.

His school studies over, he made up his mind to pursue natural science as a career, and he even mapped out a programme for the methodical study of the principles of *all* branches of science in what he afterwards called the "naïve confidence of youth." But, however much he may have had to curtail his educational ambition, he completed during the next few years a full medical course, he studied chemistry in the laboratory of Pelouze, and passed the University examinations for Bachelier and Licencié-ès-Sciences. To carry out this programme he took a small lodging in the Rue de l'Abbé de l'Epée, and attended the school of M. Crouzet. In this school happened that fortunate meeting between Berthelot and Ernest Renan—the beginning of a friendship which became from that day a principal element in the lives of both. Renan, then twenty-two, had renounced his clerical orders, and retired from Saint Sulpice. Lonely and depressed by his mental struggles, he had become an assistant master in the school, but could not shake off his melancholy. Berthelot spoke to him, the talk became intimate, something in each ardent nature was touched and responded, and the two were drawn together until soul reacted with soul like acid and alkali. "Our friendship," wrote Renan, "was something analogous to that of the two eyes when they fix upon the same object, and from the two images there results a single impression in the brain." Renan and Berthelot would take long walks together, and on Sundays would visit Neuilly, then in the country, where Berthelot's parents had taken a house, and there they discussed the eternal problems that torture the human mind. One day Renan called his young friend a "Revolutionist." But Berthelot had one sure faith, built on the ruins of other beliefs. "I a Revolutionist?" he cried, "clear your mind of that notion; call me rather an 'Evolutionist.'" We must remember that this was said a decade before Darwin gave us the "Origin of Species."

The ideas resulting from their stimulating intercourse took different shapes in the two minds, and though Renan admitted his indebtedness to Berthelot, it is impossible for us, as it was for them, to separate what was due to each. On the monument of Berthelot

which is to be placed in the Gardens of the Luxembourg, the sculptor, Saint Marceau, has introduced the face of Renan as a memorial of one of the most notable friendships of our time.

Under Pelouze the experimental skill of the young chemist rapidly developed, and in 1850 he presented his first paper to the Academy of Sciences—"On a simple method of demonstrating the liquefaction of gases." He showed how the gases chlorine, ammonia, and carbon dioxide could be liquefied in the capillary end of a glass tube by the expansion of mercury filling the body of the tube. When oxygen and nitric oxide showed no sign of liquefaction under pressures of 700 to 800 atmospheres he rightly concluded that under certain conditions of temperature it was not possible to liquefy gases by pressure alone. A second paper appeared in the same year, and in January, 1851, Berthelot received his first appointment, that of lecture-assistant to Balard, the discoverer of bromine, then Professor of Chemistry in the Collège de France. Unluckily the stipend was not a living wage—800 francs (£32) a year—and to earn a living Berthelot had to give private lessons. Luckily the official duties of the post were not heavy, and the resources of the laboratory were placed freely at his disposal by Balard, who in proposing him for the post wrote: "Everything allows us to hope that M. Berthelot will know how to utilise for the advancement of science the position I ask for him." In three years from his appointment Berthelot had obtained his degree by his remarkable thesis, "On the combinations of glycerine with acids, and on the synthesis of the immediate principles of fats." A year later he began to publish his work on the sugars, and the same year (1855) made the memorable syntheses of ethyl alcohol from ethylene, and of formic acid from carbon monoxide, which revolutionised the accepted ideas on the formation of organic compounds. Then followed in quick succession researches on the synthesis of hydrocarbons, of methyl alcohol, and of oxalic acid. After eight years' brilliant work, Berthelot was appointed Professor in the École Supérieur de Pharmacie, where he lectured, but he continued to act as assistant and to research in the Collège de France. This was the first public recognition of his discoveries. Early in the following year (1860) this Society honoured itself and him by electing him a Foreign Member. At the invitation of Alexander Williamson, then President, Berthelot lectured before the Chemical Society "On the synthesis of organic substances," on June 4th, 1863. It is pleasant to think that our Chemical Society set, rather than followed, the fashion.

With the appearance of his first book, "Organic Chemistry founded on Synthesis" (1860), the fame of Berthelot quickly spread

the Jecker Prize was awarded to him in 1861 by the Academy of Sciences. The professors of the Collège de France, headed by Balard, petitioned the Minister of Public Instruction to found a Chair for Berthelot, and this movement resulted in his being appointed to a Professorship in the College in 1861, and finally (August, 1865) in the formation of a special Chair of Organic Chemistry, which Berthelot held until his death. But though his early academic promotion was slow, honours came thickly to him in his middle age. The French Academy of Medicine elected him a member in 1863; he was elected to the Academy of Sciences in 1873, and of this body he succeeded Pasteur as Perpetual Secretary in 1889. In 1900 he became one of the forty French Academicians. I cannot attempt any enumeration of the various learned societies of which he became an honorary fellow; I will only mention that he was elected a foreign fellow of our Royal Society in 1877, and that a Davy Medal was awarded in duplicate to him and to his friendly rival in thermochemistry, Julius Thomsen, in 1883, and that he received the Copley Medal, the highest distinction the Royal Society has to bestow, in 1900.

On his appointment to a Professorship in the Collège de France, Berthelot was enabled to fulfil his engagement to Mademoiselle Sophie Caroline Niaudet, niece of M. Louis Breguet, a French savant whose family had been prosperous manufacturers of scientific instruments for many years, and who himself was the constructor of a well-known telegraph and induction coil. The story goes that the Berthelot and Breguet families had been intimate for some years, but Marcelin had not lifted his eyes to the beautiful Mademoiselle Sophie until one day accident brought them into collision on the Pont-Neuf. She was crossing the long bridge in front of Berthelot, and making her way with difficulty in the teeth of a strong wind, when a stronger gust catching her skirt and crinoline blew Mademoiselle round into the arms of her future husband.

They were married on May 10th, 1861. Never was a happier match, or a more devoted family than Berthelot's. Madame Berthelot was endowed above most women with grace, with tact, and with sympathy; she brought into his life that great gift of serenity which Berthelot regretted he had not inherited from his mother. Well might he have appreciated our homely English saying, "It's an ill wind that blows nobody any good."

Busy in his laboratory by day and in his study by night, Berthelot took little part in public life under the imperial régime until the overthrow of Louis Napoleon and the siege of Paris in 1870. Then he threw himself whole-heartedly into the work of resisting the

invaders, and as president of the Scientific Committee of National Defence superintended the manufacture of explosives to be used against the enemy. After the war Berthelot continued the study of explosives, to which he applied all his experimental skill and the knowledge he had acquired in his thermochemical researches. In collaboration with Vieille he began a systematic investigation of the phenomena of explosions, which finally resulted, not only in the invention of a powder that gave to French arms for some years a remarkable superiority, but in the addition to science of a new chemical constant—*l'onde explosive.*

His work on the combination of nitrogen with organic bodies under the influence of the silent electric discharge turned his attention to the fixation of nitrogen by plants in the soil; in 1883 a laboratory was built for him on the heights of Meudon, and there he devoted himself every summer to problems of vegetable chemistry.

Determined to take his share in the government of his country, he was elected a Permanent Senator in 1881, and in 1886 became Minister of Public Instruction in the Cabinet of M. Goblet. Here he found the opportunity of impressing on his generation his strong convictions on the educative and liberalising power of science. But he was no advocate of an illiterate mechanical training; he held firmly that science should be taught on the broad basis of a literary culture. It was in this spirit that he met the demand for "technical education" which swept over Europe. Industry demands two things, according to Berthelot: capable directors and competent workers. To be capable the director must be a judge of men and a judge of things; he must be trained in literature, history, and science; the high school and the university will prepare him for his business. To be competent the worker must be intelligent and skilful; the elementary school and the workshop will fit him for his job. Berthelot saw no need for ordinary technical schools—except as evening schools to help the workman. Can we yet say that Berthelot was wrong? At all events, he knew what he wanted, and he helped France to get it.

In 1895 Berthelot accepted the Portfolio of Foreign Affairs in the Bourgeois Cabinet. In this difficult post he had to negotiate the Anglo-French treaty dealing with the status and boundaries of Siam, which found herself in the uncomfortable position of "buffer" state between the French in Annam and the English in Burmah. Berthelot did not feel the duties of the Foreign Office congenial, and he resigned shortly after signing the treaty with Great Britain. But this, I think, we can say—that as a politician he had a sincere regard for England, and had he continued to guide the foreign relations of France the *Entente*, that has happily smoothed away

to many difficulties between the two nations, might have blossomed a decade earlier.

That Berthelot was a man of peace is evident from his book, "Science et Libre Pensée." It contains a strong plea for international arbitration. Of his other books mention must be made of his studies of the Greek and Arabian alchemistic writings. In 1869 Berthelot visited Egypt, where his imagination was struck with the early records of chemical and metallurgical experiments and ideas. He returned to this subject later, and followed it up with his characteristic eagerness. By his influence he obtained the publication of many rare manuscripts on alchemy, which he edited in collaboration with M. Ruelle, "Collection des Alchimistes Grecs," and with MM. Duval and Houdas, "La Chimie au Moyen-Age."

Few more interesting chemical papers have ever been published than the hundred and one preparations and recipes comprised in the Papyrus of Leyden translated by Berthelot. They reveal some of the methods of the Egyptian priesthood, who were the holders of the secrets of chemistry. How pithily is described the conversion of a copper vessel into a beautiful vase of gold (by rubbing it with gold amalgam and heating)—a vase which will stand the regular test of the touch-stone! With what cynical pleasure Berthelot remarks that such a fraud was no doubt quite natural, and even commendable in the eyes of a priest!

In 1880 it was my great privilege to be introduced to Berthelot in his laboratory at the Collège de France by Sainte-Claire Deville and Alexander Williamson. I had just been showing for the first time non-explosive mixtures of dried carbon monoxide and oxygen at the British Association Meeting at Swansea. Deville was enthusiastic over the discovery, since it upset one of our cherished ideas; but Berthelot was more philosophical. Carbon monoxide was a gas, he said, "a little capricious" in its ways. One must repeat and again repeat such experiments. Most sound advice! I had, by the way, been repeating these experiments for four years before I published them; and it was in "again repeating" them that, all unconsciously, I struck across one line of Berthelot's own work—the measurement of the rate of explosion in gases.

But except for this natural attitude of philosophic doubt Berthelot was kindness itself. We were taken to his home in the Institute, and were entertained by Madame Berthelot, whose silver hair heightened the saint-like beauty of her face. Berthelot was full of fire and quick replies. When Williamson rallied him on the rapidity with which his memoirs appeared, Berthelot replied, "Ah! you English are too cautious, too frightened of committing your-

selves; what is worth doing is worth publishing!" It was perhaps characteristic of him that an hour before he had given me the opposite and better advice.

Those who met Berthelot in his prime could not but be struck with the intellectual sincerity and the intense enthusiasm of the man. The broad forehead, the brilliant, blue eyes, the clear-cut features, and the thoughtful expression impressed all who saw him, while his musical voice and clear enunciation charmed the ear. It would be impossible to forget that first impression.

Students who attended his lectures speak in the highest terms of the inspiration they drew from his teaching. He gave of his best, and delighted to show his audience the new experiments he was engaged upon. But it was when he forgot the immediate experiment in hand, and began to think aloud, that the inspiration was highest. Here truly was science "in the making."

(2) *His Scientific Work.*

In considering the amazing output of scientific work we owe to Berthelot, it would be useless to enumerate, and hopeless to discuss individual memoirs. Luckily they can be grouped into well-marked divisions, for Berthelot always followed up a train of thought until some logical explanation was reached that satisfied his mind. Then some idea suggested by the first research was followed up experimentally until another generalisation was reached, and other trains of thought could be pursued.

Study of Glycerine.—As soon as he was installed in Balard's laboratory in the Collège de France, Berthelot took up a line of research which led him on to discoveries of the highest interest. He began to study the modes of combination of glycerine with acids and proved that it was an alcohol capable of combining with acids to form "etherial salts"—thus bearing out the views of Chevreul that fats were "compound ethers," and justifying the modern name "glycerol"; but he also showed that glycerol differed from ordinary alcohol by its ability to combine with three equivalents of an acid instead of with one, just as phosphoric acid differs from nitric acid in combining with three equivalents of a base. By what seems a curious mental slip Berthelot likened the three classes of esters formed by glycerol to ortho-, para-, and meta-phosphates, instead of to their true analogues, the three salts of ortho-phosphoric acid. Wurtz not only made the correction, but by his synthesis of glycol—the "diatomic" intermediate between the "monatomic" alcohol and the "triatomic" glycerol—confirmed the importance of Berthelot's discovery. The work of Berthelot and Wurtz on the

elyatomic alcohols must rank in importance with that of Liebig s the organic polybasic acids. I think, also, it is clear that the nalogies shown by alcohols to inorganic bases—and I may specially ention the analogy between glycerol and bismuth hydroxide ointed out by Odling—led to the general adoption of the idea of alency which had been given to chemistry by Edward Frankland. he proof that glycerol is an alcohol led Berthelot to prepare and xamine many other bodies of a like nature. We are indebted to erthelot for a considerable number on the list of substances recognised as alcohols, and we constantly employ his method of etylisation as the means of recognition.

Synthesis of Organic Substances.—I can only make a passing ention of very few of the many compounds of glycerol prepared y Berthelot by submitting it to the action of acids. Hydriodic id, he found, yielded two substances, *iso*propyl iodide and allyl lide; from the latter he made for the first time artificial oil of ustard.

The curious reducing power of hydriodic acid, especially at a high mperature, he afterwards made good use of in reducing benzene-hexane-derivatives (1867). But the most stimulating thing to rthelot's mind was the discovery that glycerol would combine, if ne were given it, with all sorts of different acids, producing new tty bodies, and that one could predict the formation of an endless mber of new substances through a "creative power greater than at realised in nature." This idea, once planted in his mind, ew apace. He sought and found methods for preparing the mpler types of organic compounds, and from these to pass on the higher and more complicated. To appreciate the boldness Berthelot's conceptions we must remember the firm conviction at chemists held throughout the first half of the last century, that re was a gulf fixed between inorganic and organic substances; chemist might build up, or synthesise, inorganic salts, but he uld only break down, or analyse, the substances created in plants d animals by the "vital force." This gulf had not been really sed in the eyes of most chemists by the synthesis of urea by hler or the formation of acetic and propionic acids from their riles by Kolbe and Frankland, for the cyanides from which these stances were formed were regarded as organic products mselves.

Berthelot's first success on his new path came in 1855. He shook pure sulphuric acid in a large globe holding 32 litres of ethylene until 30 litres of the gas had been absorbed. The liquid was n mixed with water and distilled. The liquid coming over was ed and redistilled until 45 grams of a liquid having all the

properties of pure alcohol were obtained. But the original ethylene had itself been obtained from alcohol—so the synthesis might be said to be contaminated at its source. Berthelot next prepared ethylene iodide from coal gas, and from this prepared a sample of ethylene, which he treated as before. It yielded alcohol, which was thus made for the first time without fermentation.

Now since ethyl alcohol on heating with sulphuric acid yields ethylene and water, and formic acid on heating with sulphuric acid yields carbon monoxide and water, if the first process can be reversed, it might be predicted that the second would also:

$$C_2H_6O = C_2H_4 + H_2O.$$
$$CH_2O_2 = CO + H_2O.$$

Berthelot placed 10 grams of potash in a half-litre flask, which he filled with carbon monoxide, sealed, and heated for three days in a water-bath. When the flask was opened under mercury the gas was found to be completely absorbed; on dissolving the potash salt in dilute sulphuric acid and distilling, Berthelot obtained a distillate of formic acid.

In the following year (1856) a more difficult synthesis was effected—that of marsh gas, together with ethylene and acetylene. Formic acid on heating yields all its carbon as carbon monoxide and its hydrogen as water; but if there is present a strong base, which might cling to some of the carbon, a substance containing carbon and hydrogen might be evolved. Berthelot prepared formic acid on a large scale from carbon monoxide, combined it with baryta and distilled the barium formate at a red heat. He condensed a small amount of liquid, caught the unsaturated hydrocarbons in bromine, and collected the marsh gas over water. The unsaturated hydrocarbons were ethylene and propylene. On decomposing the bromides by means of water and copper foil in thick glass tubes at 275°, Berthelot regenerated the ethylene and propylene and found about 10 per cent. of acetylene—the result of a secondary action. From this ethylene he again prepared pure alcohol.

Berthelot's next starting point was carbon disulphide. If carbon disulphide were heated with a metal capable of combining with the sulphur, while at the same time hydrogen were liberated in contact with the nascent carbon, the two might combine to form a hydrocarbon. Passing hydrogen sulphide and carbon disulphide vapour through a broad tube packed with copper turnings freshly reduced and heated to a dull red heat, Berthelot condensed a trace of naphthalene, and collected ethylene in bromine and marsh gas over water. Iron acted in the same way as copper, and hydrogen phosphide and steam could be used instead of hydrogen sulphide

Berthelot regenerated the ethylene as before (finding acetylene produced), and prepared alcohol from it. One cannot help feeling in reading Berthelot's account of this experiment that in his mind the ethylene (with its resulting alcohol) was more important than the marsh gas. But a year later Berthelot chlorinated marsh gas in diffused daylight, separated the methyl chloride from the residual marsh gas and higher chlorides by solution in anhydrous acetic acid, and prepared methyl alcohol from the chloride.

Just as Berthelot had got ethyl alcohol from ethylene and ...phuric acid, so he obtained propyl alcohol from propylene and ...phuric acid. The propylene was prepared from the propyl ...dide obtained from glycerol and phosphorus iodide. Again he ...owed that the higher olefines could be combined with hydrogen ...oride and the chlorides turned into the corresponding alcohols— ...general method by which he prepared many alcohols; and *vice ...ersâ*, by abstracting the elements of water the olefines could be ...epared from the alcohols. Again, as barium formate yielded ...n distillation several hydrocarbons, so might the acetate of sodium ...ield other hydrocarbons than marsh gas. Berthelot found that it ...elded higher olefines as well, namely, propylene, butylene, and ...ylene.

But among the most memorable of Berthelot's syntheses was the ...rect combination of hydrogen and carbon in the electric arc to ...rm acetylene (1862), and the condensation of acetylene into ...nzene (1866); thus the barrier between inorganic and organic ...emistry was broken down at all points, and Berthelot's disciples ...uld exclaim with justice: "There is but one chemistry, and ...rthelot is its prophet."

In working on acetylene Berthelot investigated the properties of ...e acetylides of silver and copper. This work led him in 1866 to ...ake the suggestion that the mineral oils found in the earth might ...ve been formed from acetylene produced by the action of water ...d carbonic acid on the acetylides of the alkali metals. By ...ducing the carbonaceous matter found in meteorites he produced ...e liquid petroleum.

...ction of Heat on Hydrocarbons.—Berthelot's work on the hydro...rbons included a study of the mode in which these bodies behave ...a red heat. A hydrocarbon, he says, is not directly resolved into ...elements, but either polymerises (for example, acetylene into ...nzene) or by a condensation of two or more molecules forms a ...ser hydrocarbon with elimination of hydrogen; thus marsh gas ...es mainly acetylene and hydrogen, ethane yields ethylene and ...drogen, while ethylene yields mainly acetylene and hydrogen. ...etylene itself is not resolved into its elements, but polymerises,

or condenses with hydrogen or other hydrocarbons into compounds of great density—naphthalene, anthracene, etc. When carbon is finally separated, it is therefore not a simple molecule, but in the form of a highly complex group of atoms corresponding with the dense hydrocarbons yielding it. This attractive theory of Berthelot has not, however, been fully borne out by later work. Sir Edward Thorpe showed that the decomposition of a paraffin (under heat and pressure) gave rise to the formation of an olefine and a lower paraffin; and Haber showed that *n*-hexane gave methane and amylene, but confirmed Berthelot's observation that benzene condensed to diphenyl with loss of hydrogen. Bone and his colleagues have shown that methane is formed directly from its elements between 1000° and 1200°, and breaks up again into carbon and hydrogen without forming acetylene. Ethylene, on the other hand, gives acetylene, which itself can either recombine with hydrogen or break down into carbon and hydrogen.

Action of Mass.—The observation made by Berthelot that time was required for the union of glycerol with acids led him, in conjunction with his pupil, Péan de St. Gilles, to investigate the course of the reaction between alcohols and acids, especially that between ethyl alcohol and acetic acid. Here, again, Berthelot was a pioneer in a subject that had hardly been touched experimentally. He found that when equivalent amounts of alcohol and acid are brought together, the reaction proceeds slowly (at a rate depending on the temperature) until a limit is reached, and that the same limit is reached when the corresponding amounts of ester and water are brought together. "An equilibrium is established between the affinity of the acid for the alcohol, which tends to unite them, and the inverse affinity of the water for the neutral ether, which tends to regenerate the acid and the alcohol." We can put the result into an equation:

$$\frac{C_2H_8O_2{\cdot}C_2H_5 \times H_2O}{C_2H_4O_2 \times C_2H_6O} = 4.$$

It is clear, I think, that Berthelot regarded the equilibrium as a statical, and not as a dynamical, one; he did not see that the two opposite reactions were taking place at the same time: Guldberg and Waage recognised this, and used Berthelot's figures in illustration of their principle. Nevertheless, Berthelot and St. Gilles's memoirs form the starting points of much of the subsequent work on equilibrium and mass action. They showed the effect on the equilibrium of varying the amounts of one of the reacting substances; they showed that an increase of temperature or of concentration greatly shortened the time for the equilibrium to be

reached, although pressure alone had little effect. They suggested an equation for the determination of the velocity of a bimolecular reaction similar to that of Harcourt and Esson. Few researches indeed have been more fruitful in physical chemistry than those of Berthelot and St. Gilles. *

Of other equilibrium problems Berthelot was the first to investigate the partition of a dissolved substance between two solvents. He showed, for instance, that when succinic acid is dissolved in ether and water, the coefficient of distribution is constant whatever the amounts dissolved; but other substances showed a variation with concentration, an anomaly explained by Nernst in 1891 as due to a difference of the molecular aggregation of the substance in the two solvents. In 1875 Berthelot studied the partition of acids between several bases in solution.

Thermochemistry.—Berthelot's great work on thermochemistry was begun in 1863, and was continued until 1879, when he published the two volumes entitled, "Mecanique Chimique fondée sur la Thermochimie." This and his later book, "Thermochimie, Données et Lois numériques," constitute a monument of elaborate experiment and calculation, which men of science rank alongside the "Thermochemische Untersuchungen," the life-work of Julius Thomsen. It is not at all to the disadvantage of Chemistry that the Frenchman and Dane worked in rivalry. When we want to know the heat of formation of any compound we look up the two authors, and if they agree we are entirely satisfied. I think each respected the other's work. I can point to an instance—the heat of formation of ammonia—where Thomsen corrected his first result, and to another—the heat of formation of ethane—where Berthelot corrected his; in each case as the result of the other's work. They both put forward a theorem, though not quite in the same terms, that every action of a purely chemical nature gives out heat and produces the result that is accompanied with the maximum evolution of heat. Berthelot defended with great skill his "principle of maximum work", it required the genius of Helmholtz and Boltzmann to prove that the principle required that the heat of reaction should be independent of the temperature, and was only strictly true at absolute zero. But although these limitations must be accepted, and Berthelot finally accepted them, the "law" is nevertheless a useful guide which is often appealed to. Was not Deacon inspired by Berthelot's ideas when he sought and finally found a practical method of liberating chlorine from hydrochloric acid by the oxygen of the air?

Much of the apparatus devised by Berthelot for his thermo-

chemical determinations has come into general use; in particular I may mention his "calorimetric bomb" for combustions in oxygen under pressure.

Explosions.—Berthelot's experiences in the war led to his systematic work on explosives and on the theory of explosions. In conjunction with Vieille he studied the rapidity of combustion and the heat of reaction of various explosives. In July, 1881, he published his first short paper on the explosion-wave in gases. He states that he would not have published it had not MM. Mallard and Le Chatelier sent him their memoir on the same subject, which they had attacked by a different method. It is a curious coincidence that a few months before I had myself begun to measure the rate of explosion of carbon monoxide and oxygen with different quantities of water-vapour, and found that the accepted rate was altogether too slow.

Berthelot's first paper contains the germ of his theory of the identity of the rate of explosion with the mean velocity of the molecules formed in the reaction before any heat had been lost. Other papers quickly followed. Berthelot made the important discovery that the rate of explosion rapidly increased from the point of origin until it reached a maximum which remained constant however long the column of gases might be. This maximum Berthelot stated to be independent of the pressure of the gases, of the material of the tube, and of its diameter above a small limit. The rate of explosion thus forms a new physico-chemical constant having important theoretical and practical bearings. The name "l'onde explosive" was given by Berthelot to the flame when propagated through an explosive mixture of gases at the maximum velocity, and this velocity could be predicted if the heat of combustion and the density and specific heat of the products were known. For instance, the total heat given out when hydrogen and oxygen combine is known. If this heat is contained in the steam produced, its temperature may be calculated if its heat capacity be known, and if the temperature of the steam be known, the mean velocity with which the molecules must be moving can be calculated. Now Berthelot supposed that the heat is all contained in the steam produced. He assumed that the heat capacity of steam was the same as the sum of those of its constituents; and he supposed, moreover, that the steam was heated at constant pressure. Making these assumptions, he calculated out the theoretical mean velocity of the products of combustion of various mixtures, and found a close accordance between these numbers and the explosion rates of the same mixtures. He concluded that the explosion-wave was propagated by the impact of the products of combustion of one layer

pon the unburnt gases in the next layer, and so on to the end of tube at the rate of movement of the products of combustion emselves. If this theory be true, it accounts, not only for the treme rapidity of explosion of gaseous mixtures, and gives the eans of calculating the maximum velocity obtainable with any ixture of gases, but it also affords information on the specific heats gases at very high temperatures, and explains the phenomena detonation whether of gases or of solid or liquid explosives.

Table I shows the explosion rates found by Berthelot, compared ith the theoretical velocity of the products of combustion:

TABLE I.

Gaseous mixture.		Velocity in metres per second. Calculated.	Found.
Hydrogen and oxygen	$H_2 + O$	2830	2810
Hydrogen and nitrous oxide	$H_2 + N_2O$	2250	2284
Carbon monoxide and oxygen	$CO + O$	1940	1090
Carbon monoxide and nitrous oxide	$CO + N_2O$	1897	1106
Marsh gas and oxygen	$CH_4 + O_4$	2427	2287
Ethylene and oxygen	$C_2H_4 + O_6$	2517	2210
Cyanogen and oxygen	$C_2N_2 + O_4$	2490	2195
Acetylene and oxygen	$C_2H_2 + O_5$	2660	2482

Two facts established by these experiments impressed on me the nviction that Berthelot might have found the true theory of plosions: first, the close coincidence between the rates of explosion hydrogen (both with oxygen and nitrous oxide) and the calculated an velocities of the products of combustion; and, secondly, the eat discordance between the found and calculated rates for rbonic oxide with both oxygen and nitrous oxide, for I had eviously discovered that pure carbon monoxide cannot be ploded either with pure oxygen or pure nitrous oxide. The dis-rdance found by Berthelot was what I should have expected from own experiments. Again Berthelot examined the effect of inert ses in damping down the velocity of the explosion-wave; for stance, on adding nitrogen to different explosive mixtures he und

TABLE II.

Gaseous mixture.	Velocity in metres per second. Calculated.	Found.
$H_2 + O$	2831	2810
$H_2 + O + N_2$	1935	2121
$H_2 + O + 2N_2$	1820	1439
$CH_4 + 2O_2$	2427	2287
$CH_4 + 2O_2 + 2N_2$	2002	1858
$CH_4 + 2O_2 + 4N_2$	1744	1151
$C_2N_2 + 2O_2$	2490	2195
$C_2N_2 + 2O_2 + N_2$	2334	2044
$C_2N_2 + 2O_2 + 2N_2$	2152	1208

These experiments seemed to Berthelot to show that a small amount of inert gas does not prevent the propagation of the true explosion-wave, but damps it down according to its calculated effect. A large amount of inert gas, on the other hand, destroys the character of the explosion-wave—which must always be regarded as the "*maximum possible*" velocity.

In comparing the rates of explosion determined in his tubes with those calculated from his formula, Berthelot, I think, was not justified in his argument that the specific heats of the gaseous products must be reckoned as at constant pressure, since the whole change took place in a closed tube. In the damping experiments with nitrogen he did not allow for the fact that with inert gases a longer run is required before the explosion-wave is set up, and he began to time the flame before it had acquired its maximum pace. In the cyanogen experiments he did not appreciate the fact that in the wave-front the carbon only burns to carbon monoxide. But in spite of these criticisms, which required years of work to establish, I have always thought it one of Berthelot's strokes of genius to identify the maximum velocity of the flame with the mean translational velocity of the molecules themselves, a conception which all later investigators have used in working out the propagation of an intense pressure-wave which preserves its type by being continually reproduced from point to point by the chemical action.

Fixation of Atmospheric Nitrogen.—In Berthelot's synthetic researches we find him using the silent electric discharge to cause nitrogen to enter into combination, for example, as in the direct formation of hydrocyanic acid from acetylene and nitrogen. The fixation of nitrogen led him to investigate its absorption by plants and generally the action of electricity on vegetable growth in his laboratory at Meudon. Berthelot asserted that free nitrogen could be assimilated by plants, a statement that was vehemently opposed until Hellriegel proved that leguminous plants can take up nitrogen through the agency of bacteria. Berthelot was the first to point out that atmospheric nitrogen was fixed in the soil by micro-organisms, a new departure of supreme interest to agriculture. Among other developments of Berthelot's idea, Dr. E. J. Russell has recently shown how the fertility of a soil might be enormously increased by killing off the infusorial enemies of these bacteria. Four solid volumes, entitled, "La Chimie végétale et agricole," published in 1899, contain the record of Berthelot's work at Meudon.

Looking back at the enormous mass of experimental data published by Berthelot I am astonished at the small percentage of

error that has been detected. The accuracy of his experiments is really marvellous. It is not in his experiments, but in his interpretation of them that Berthelot has to meet criticism. Although Berthelot was a rapid worker, he was a still more rapid thinker. Not once or twice, but almost throughout the range of his researches we see the theoretical conception outstripping the experiment. Sometimes deliberately, sometimes unconsciously, he chooses his experiments to illustrate his theory. It is a question of idiosyncrasy, genius must work its own way. The nineteenth century praised Dalton for basing his Atomic Theory on the sure foundation of the Law of Multiple Proportions; the twentieth century knows that Dalton sought for cases of multiple proportion to support his preconceived theory of atoms.

Berthelot's imagination gives a distinction to all his work; his quality of generalisation fascinates us, and compels our interest. Can we say which is the better for knowledge—on the one hand, the dashing advance of an explorer into an unknown country, the rapid survey, the approximate location of a great lake and a great mountain range, and the publication of a fascinating sketch-map showing us the possible sources of a Nile or a Congo; or, on the other hand, the deliberate advance of a surveyor with his levels and theodolites? May it not with justice be maintained that had it not been for the pioneer and his map the surveyor would never have started at all? Berthelot might rightly claim that he had pointed out the trend of the country and the possibilities that lay that way, and had stimulated the curiosity of the exploring world. "For myself," he wrote, "I shall be happy if, in the development of science, some of my results are valued some day as the origin of the discoveries of the future." I believe this was no conventional phrase of self-depreciation, but an expression of his thought used in all sincerity.

Again, like other great men, Berthelot found it hard, even when the creatures of his thought had been proved to be "unemployables," to dismiss them from his service. I ventured just now to compare Berthelot's mode of thought with Dalton's. May we extend the parallelism further, and say that the intensity of conception in the mind of each was sometimes too strong to yield to facts? Dalton, firm in his conviction that different elements had atoms of different sizes (the very genesis of his theory), could see neither the relevancy of Gay-Lussac's Law of Volumes nor the beauty of Avogadro's explanation. For him the formula of water was always HO. Berthelot, equally firm in his conviction that in chemical reactions we are dealing with "equivalents," could see the force of Gay-Lussac's experiments, but not of Avogadro's argument. For him

the formula of water (the molecule occupying 2 volumes), viz. H^2O^2.

If we, then, as the result of the steady progress of experiment and thought, can see the limitations of Berthelot's vision, we can also, I hope, appreciate the brilliancy of the conceptions that guided his work, and the intensity of the stimulus given by his ideas to contemporary science.

(3) *The Last Phase.*

Berthelot enjoyed a wonderfully active and honoured old age. To celebrate his seventy-fifth birthday and the jubilee of his first appointment in the Collège de France, his colleagues inaugurated a great meeting of congratulation, and commissioned M. Chaplain to design a medal in his honour.

The Chamber of Deputies and the Senate declared that the occasion demanded a public ceremonial, in which the State should participate. Abroad, all the great societies passed resolutions congratulating Berthelot on his achievements, and sent delegates to present their felicitations in person. The meeting was held in the great hall of the Sorbonne on November 24th, 1901. Berthelot declined the procession and the military escort offered by the State and went on foot to the hall. He was received by the President of the Republic. Then amid the acclamation of his colleagues, who thronged the hall, he heard perhaps for the first time from the mouths of his most distinguished contemporaries the deep veneration in which the world held his genius and his career. In acknowledging this great demonstration, Berthelot once more insisted on the humanising spirit of science. "It is not," he cried, "for the satisfaction of our private vanity that the world to-day pays homage to men of science. No! it is because it knows that the man of science really worthy of the name consecrates his life disinterestedly to the great work of our age—the amelioration of the lot of all, the rich and the happy, the poor and the suffering. It is this that my friend Chaplain has sought to express on the beautiful medal which the President of the Republic is to offer me. I know not if I have completely fulfilled the noble ideal the artist has drawn, but at least it has brought me strength to have made this the aim that has directed my life."

"*Pour la Patrie et la Vérité*"—the design was well chosen by Chaplain to sum up Berthelot's career.

Berthelot continued to work to the end. Although he ceased to lecture, he seldom passed a day without visiting his laboratory. There and in his home he found his happiness, for husband and wife seemed to grow nearer as the years went by. In his last months

he had the sorrow of losing a daughter and then a beloved grandson. The shock preyed on his wife, who developed heart disease. Berthelot, himself a victim to the same disease, watched assiduously at her bedside, and wasted his strength in his nightly vigils over her. A Sunday came when she seemed better, and Berthelot visited his laboratory at Meudon, where he was studying the effects of radium emanations on vegetation. On his work table there was found afterwards an alchemic manuscript from Morocco, written in Hebrew, which he was deciphering, for he had not forgotten the early lessons he had received from Renan.

He returned to find his wife failing, and they both knew the end was near. "What will become of him when I am no longer there?" were the last words she spoke to her daughter. Berthelot was alone with his wife when she died. He called his children, kissed the dead, walked into the next room, and threw himself upon a couch. One of his sons followed him, and hearing him sigh, ran to seize his hand. But the hand was lifeless: he had joined his beloved one.

The pagan poet whom Berthelot loved has perhaps made us feel most keenly the cry of the heart that cannot survive separation:

"Ah! te meae si partem animae rapit
Maturior vis, quid moror altera,
Nec carus aeque nec superstes
Integer? Ille dies utramque

Ducet ruinam. Non ego perfidum
Dixi sacramentum. Ibimus, ibimus
Utcumque praecedes, supremum
Carpere iter comites parati." *

The state procession and military escort which Berthelot had declined alive, were fitting attendants round the hearse that bore the bodies of husband and wife to honourable sepulchre in the Pantheon.

So passed away a great man, full of years and honour. To France and to Science he gave his life, and he was not without reward in the love and veneration of his countrymen. Happy the country that produces such genius; happier still the country that can appreciate and use it.

* At the request of the Publication Committee, I subjoin the English rendering of these stanzas I gave at the Lecture:

"If Death, untimely, snatch away
That half—ah! dearer half—my soul,
Why should this other half delay?
Could life be sweet no longer whole?

The day that strikes thee strikes us both:
Together, when thou goest, we go
Sworn comrades ('tis no idle oath)
To tread the last long path below."

—*Horace* II. xvii.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS AND PROCEEDINGS. 1911.

(Marked T. and P. respectively.)

A.

B.

D.

G.

H.

N.

O.

R.

V.

W.

Z.

INDEX OF SUBJECTS.

TRANSACTIONS AND PROCEEDINGS. 1911.

(Marked T. and P. respectively.)

Single organic compounds of known empirical formula will be found in the Formula Index, p. 2397.

B.

C.

FORMULA INDEX.

The following index of organic compounds of known empirical formula is arranged according to Richter's system (see *Lexikon der Kohlenstoff-Verbindungen*).

The elements are given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

The compounds are arranged—

Firstly, in groups according to the number of carbon atoms (thus C_1 group, C_2 group, etc.).

Secondly, according to the number of other elements besides carbon contained in the molecule (thus 5 IV indicates that the molecule contains five carbon atoms and four other elements).

Thirdly, according to the nature of the elements present in the molecule (given in the above order).

Fourthly, according to the number of atoms of each single element (except carbon) present in the molecule.

Simple metallic salts of acids are indexed under the respective acids.

Simple salts of bases (for example, hydrochlorides, platinichlorides, and picrates), when described for the purpose of further identifying the base, are indexed under the latter.

C_1 Group.

C_2 Group.

2 III

C_3 Group.

3 III

3 IV

C_4 Group.

6 III

6 IV

6 V

C_7 Group.

7 IV

C_8 Group.

8 II

8 III

8 IV

C_9 Group.

9 II

9 III

9 IV

C_{10} Group.

10 II

10 III

11 III

11 IV

C_{12} Group.

12 II

12 III

13 III

14 III

14 IV

C_{15} Group.

15 III

15 IV

C_{16} Group.

16 II

16 IV

C_{17} Group.

17 III

17 IV

C_{18} Group.

18 III

18 IV

C_{19} Group.

19 III

19 IV

C_{20} Group.

20 III

20 IV

C_{21} Group.

21 III

C$_{23}$ Group.

23 III

23 IV

C$_{24}$ Group.

24 III

24 IV

C_{25} Group.

25 III

25 IV

C_{26} Group.

26 III

26 IV

C_{27} Group.

35 III

C_{36} Group.

C_{37} Group.

C_{39} Group.

39 IV

C_{40} Group.

C_{43} Group.

43 III

C_{45} Group.

C_{51} Group.

51 III

C_{55} Group.

ERRATA.

VOL. LXXXIX (TRANS., 1906).

Page	Line	
1468	11 and 12	*for analysis read*

0·2801 gave 0·6353 CO_2 and 0·1850 H_2O. C = 61·86 ; H = 7·33.
$C_{10}H_{14}O_2N_2$ requires C = 61·9 ; H = 7·2 per cent.

VOL. XCV (TRANS., 1909).

Page	Line	
1774	22*	*for* "C_1" *read* "Cs."

VOL. XCVII (TRANS., 1910).

Page	Line	
2454	19*	*for* "a thousand" *read* "ten thousand."
2460		last number in 6th column of *viscosities* at 0° *for* "[illegible]" *read* "8703," and fourth number of 7th column of *viscosities* *for* "8236" *read* "9236."
2462		Fig. 2 for "$\sqrt{}$*normality*" read "$\sqrt[3]{}$normality."

VOL. XCIX (TRANS., 1911).

Page	Line	
451	20	*for* "acid" *read* "ester."
810	17*	,, "an acid salt, $C_8H_3O_8CuH$" *read* "a double salt, $C_8H_3O_8$[illegible]"
810	15*	,, "protocatechuate" *read* "pyrotartrate."
810	14*	,, "pyrotartrate and malate" *read* "protocatechuate and malate"
810	13*	,, "C_2" *read* "C_4."
1263	5*	,, "Citraconic acid" *read* "Itaconic acid."
1269	22*	,, "*Special*" read "*Spatial.*"
1386	14*	,, "Paul" *read* "Pauly."

* From bottom.

ERRATA (*continued*)

Line

4 *for* "39·4" *read* "32·4."

12 *alter to* "In 1865, on Menschutkin's return to St. Petersburg, he presented his."

24* *for* "RICHARD" *read* "ROBERTSHAW."

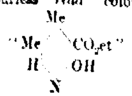
14* [illegible]

4 *delete* "normal."

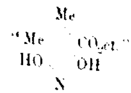
5* *insert* "=" in equation.

6 *for* "quinoid" *read* "quinonoid."

7 " "colourless" *read* "coloured."



read



* From bottom.

Organic Chemistry.

Absorption of Hydrocarbon Gases by Non-aqueous Liquids. [illegible] McDANIEL (*J. Physical Chem.*, 1911, 15, 587—610).—[illegible] of methane, ethane, and ethylene in ten organic [illegible] been determined at a series of temperatures lying between [illegible]

[illegible] burette and Ostwald absorption pipette were water-[illegible] and the temperatures were maintained approximately equal [illegible] of a suitably proportioned resistance coil in each jacket, [illegible] being in series. The gas in the burette was saturated [illegible] solvent vapour and measured at the temperature of each [illegible] experiment, so that no correction for vapour pressure of [illegible] was necessary. The solvents were boiled under diminished [illegible], and precautions were adopted to remove dissolved air, the [illegible] of which introduces considerable errors.

[illegible] solvents, in order of increasing absorptive power at 25° for [illegible], are methyl, amyl, ethyl, *iso*propyl alcohols, benzene, toluene, [illegible] hexane, heptane. With ethane and ethylene the solvents [illegible] a similar series, which, however, is quite unlike the order of [illegible] same solvents for the less soluble gases nitrogen, carbon monoxide, [illegible], and carbon dioxide.

[illegible] suggested that the solubilities of the hydrocarbon gases are [illegible] influenced by specific chemical relations with the solvents.

[illegible] absorption coefficient decreases in all cases as the temperature [illegible]

R. J. C.

Preparation of $\beta\gamma$-Dimethyl-$\Delta^{\alpha\gamma}$-butadiene. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 235311).—A 70% yield of $\beta\gamma$-dimethyl-[illegible]butadiene can be obtained by heating pinacone or pinacolin at 400° [illegible] a dehydrating agent followed by fractional distillation of the [illegible].

F. M. G. M.

Action of Di-iodoacetylene on Organic Bases. WILLIAM M. [illegible] (*J. Amer. Chem. Soc.*, 1911, 33, 1598—1601).—Di-iodoacetylene [illegible] prepared in a yield of 80—90% of the theoretical by passing [illegible] into a solution of potassium iodide and adding sodium [illegible] solution drop by drop. On mixing solutions of di-iodo-[illegible] and triethylamine in ether, the *compound*, $NEt_3,2C_2I_2$, [illegible] 115°, separates in feathery needles. Dipropylamine when [illegible] in the same way yields the *compound*, $NHPr_2,2C_2I_2$, [illegible] 160°, which forms long needles. By the action of acetylene [illegible] on phenylhydrazine, nitrogen is evolved and iodophenyl-[illegible] is produced, together with two phenylhydrazine *hydriodides*, $2NHPh\cdot NH_2,HI$, m. p. 128° (decomp.), and $NHPh\cdot NH_2,HI$, which [illegible] melt below 300°.

E. G.

Action of Alkaline Solutions on Trichlorinated Organic Compounds. G. BRESSANIN and E. SEGRÈ (*Gazzetta*, 1911, 41, i, 671—674).—Trichloro*iso*propyl alcohol (Mossler, Abstr., 1909, ...), phenyltrichloromethylcarbinol (Jocitsch, *Chem. Zentr.*, 1897, ...), and chloroform (Mossler, *loc. cit.*) yield carbon monoxide when treated with alkalis. The authors find that acetonechloroform behaves similarly, and the amount of carbon monoxide evolved indicates that the substance decomposes chiefly according to the equation

$$CCl_3\cdot CMe_2\cdot OH = COMe_2 + CHCl_3.$$

R. V. S.

Fusibility Curves of Gaseous Mixtures: Oxonium Systems Formed by Acetylene, Ethylene, Nitric Oxide, and Methyl Ether. GEORGES BAUME and ALBERT F. O. GERMANN (*Compt. rend.*, 1911, 153, 569—572. Compare this vol., i, 414; ii, ...).—The fusibility curve for methyl ether and acetylene shows a very ... maximum at $-117\cdot 1°$, corresponding with the compound Me_2O, C_2H_2. The existence of an analogous compound with ethylene is ... by the occurrence of a maximum at $-163\cdot 2°$, but this is unstable in the liquid phase. The curve for methyl ether and nitric oxide shows a maximum at $-166\cdot 3°$, corresponding with an oxonium compound, to which the constitution $\frac{CH_3}{CH_3}{>}O{<}\frac{NO}{NO}$ is ascribed.

Methyl ether has m. p. $-138\cdot 4°$.

W. O. W.

Primary Aliphatic Dinitro-, Nitro-nitrite, and Dialdoxime Compounds. JULIUS VON BRAUN and WLADISLAUS SOBECKI (*Ber.*, 1911, 44, 2526—2534).—It has been shown to be possible to apply V. Meyer's method of preparing nitro-compounds from alkyl ... to dihalogen compounds which contain the halogen atoms at ... distance from one another in the molecule. $\alpha\delta$-Dinitrobutane, ... nitropentane, and $\alpha\kappa$-dinitrodecane have been isolated and found ... stable substances. The nitro-nitrite compounds are considerably ... stable.

On cautious reduction, the dinitro-compounds are converted into dioximes, hence affording a useful method of preparing ... dialdehydes.

$\alpha\delta$-Di-iodobutane was allowed to react in ethereal solution with silver nitrite. From the product three fractions were isolated by distillation.

1. A small quantity of *butyl dinitrite*, $NO\cdot O\cdot [CH_2]_4\cdot O\cdot NO$, ... $-105°/15$ mm.

2. *Nitrobutyl nitrite*, $NO_2\cdot [CH_2]_4\cdot O\cdot NO$, b. p. about 110—115°, a liquid of ethereal odour, which soon began to decompose. On treatment with stannous chloride in hydrochloric acid solution, this compound yielded δ-hydroxybutylamine, b. p. 100°/15 mm. The dibenzoyl derivative of the latter was found to melt at 75°, whereas Hess found 58°.

3. $\alpha\delta$-*Dinitrobutane* is an almost colourless, practically odourless liquid of b. p. 176—178°/13 mm.; the *sodium* salt was analysed. Bromine transformed it into $\alpha\alpha\delta\delta$-*tetrabromo-$\alpha\delta$-dinitrobutane*, $NO_2\cdot CBr_2\cdot CH_2\cdot CH_2\cdot CBr_2\cdot NO_2$, m. p. 100°.

... iodopentane and silver nitrite gave a similar series of products. ... nitrite, b. p. 130—133°/15 mm., was found to be somewhat ... Reduction transformed it into ε-*hydroxyamylamine*,

$$OH\cdot[CH_2]_5\cdot NH_2,$$

... liquid, b. p. 122°/16 mm., which forms an oily *benzoyl* ... and a *gold* salt. The constitution of this compound was proved ... tion to piperidine by means of fuming hydriodic acid.

... *pentane* is an almost colourless liquid, b. p. 194—196°/ ... Its salts resemble those of αδ-dinitrobutane. The *sodium* ... treated with benzenediazonium sulphate yields the *com-* ... $N_2Ph\cdot CH(NO_2)\cdot[CH_2]_3\cdot CH(NO_2)\cdot N_2Ph$, m. p. 169°. ααεε-*Tetra-* ... *nitropentane* has m. p. 39°.

... *nitrodecane*, $C_{10}H_{20}O_4N_2$, m. p. 49°, was obtained by similar ... The *tetrabromo*-derivative is an oil.

... reduction with stannous chloride in hydrochloric acid solution, ... pentane gives glutardialdoxime, m. p. 178° (Harries, Abstr., ... 561, gives 171°); dinitrobutane gives succindialdoxime, and ... decane furnishes ακ-*dioximinodecane*, m. p. 137—141°.

H. W.

Anhydrous Formic Acid. JAMES B. GARNER, BLAIR SEXTON, and ... PARKER (*Amer. Chem. J.*, 1911, 46, 236—240).—Attention is ... to the lack of agreement in the values given by previous ... gators for the physical constants of formic acid. The methods ... hitherto employed yield only a 97—98% acid.

The anhydrous acid is best prepared by distilling the ordinary acid ... anhydrous copper sulphate under a pressure of 120 mm. It has ... b. p. 50°/120 mm., 99·7°/741 mm.

The density and viscosity of the pure acid have been determined at ... ratures varying from 10° to 40°: D^{15} 1·2260, D^{20} 1·2200.

F. B.

Soy Bean Oil. HERMANN MATTHES and A. DAHLE (*Arch. Pharm.*, ... 249, 424—435. Compare this vol., i, 858).—The oil contains ... of fatty acids in the form of glycerides. The fatty acids ... palmitic 15%, oleic 56%, linoleic 19%, and linolenic 4·8% approximately (compare Lewkowitsch, *Oils, Fats, and Waxes*, 1909, ... and Keimatsu, this vol., i, 766).

The two oils examined were "refined" and "unrefined," and gave ... following constants respectively: D^{15} 0·9260 and 0·9265; solidifying point −11·5°, −12°; n_D^{20} 1·468, 1·468; $[\alpha]_D$ 0°, 0°; acid number ..., 1·713; saponification value 192·3, 194·3; Hehner number ..., 95·52; iodine value 131·3, 132·6; Reichert-Meissl value ..., 0·7543; Polensky number 0·7843, 1·0784. Both oils gave ... elaidin reaction. The two oils were exposed to (1) damp air, (2) dry ..., (3) oxygen, (4) damp oxygen during six months, and then examined. The results indicated that (1) moisture raised the acid number, (2) oxygen alone or in presence of moisture did not lower the iodine value, whilst (3) damp air reduced the iodine value from 131·3 to 122·5 and from 132·6 to 105·4 for the refined and unrefined ... respectively.

Farnsteiner's process applied to the mixed fatty acids gave a fine separation of palmitic acid, but the mixed unsaturated acids thus obtained still contained some saturated acid. Bremer's method gave a bad separation of saturated acid, but the mixed unsaturated acids obtained contained less palmitic acid than the product obtained by Farnsteiner's method. No separation of components of the mixed unsaturated acids could be effected by fractional distillation, and recourse was had to bromination, and a method is described for the successive separation of linolenic acid hexabromide, linolic acid tetrabromide, and oleic acid dibromide from the mixture. T. A. H.

Preparation and Properties of α-Linolenic Acid from Linseed Oil. Ernst Erdmann (*Zeitsch. physiol. Chem.*, 1911, 74, 179—197).—The acids obtained by the hydrolysis of linseed oil are freed from the solid acids at −18° in the presence of petroleum, and the residual liquid acids are converted into their zinc salts by trituration with freshly precipitated basic zinc carbonate. By treating the salts with alcohol, the easily soluble zinc α-linolenate is removed, and from it pure α-linolenic acid obtained in 16 [illegible] calculated on the liquid acids. The acid, the purity of which is controlled by its iodine number, 269—278, and by its quantitative conversion into the hexabromide, m. p. 179°, is an unstable, somewhat mobile liquid, D_4^{20} 0·9046 (after a few days, D_4^{20} 0·9248); the zinc salt, $(C_{18}H_{29}O_2)_2Zn,\frac{1}{2}ZnO$, m.p. 72—73°, *ammonium*, *barium*, *sodium*, and basic *copper* salts are described. The acid yields *trichlorotri-iodostearic acid*, $C_{18}H_{30}O_2Cl_3I_3$, m. p. 146°, with iodine chloride, and *tribromotri-iodostearic acid*, m. p. 124—126°, with iodine bromide, and is converted by ozone into an *ozonide peroxide*, $C_{18}H_{30}O_{12}$, which is decomposed by cold water, yielding hydrogen peroxide and a semi-solid mass consisting probably of the semialdehyde of azelaic acid and malondialdehyde.

The paper concludes with a reply to Rollett (this vol., i, 17[illegible]) [illegible] is very questionable whether β-linolenic acid is present in linseed oil, although there is no doubt that it constitutes the chief ingredient of the mixture of acids obtained by the debromination of α-linolenic acid hexabromide. [illegible]

Keto-enolic Tautomerism. III. Tautomerism of Ethyl Acetoacetate. Kurt H. Meyer and Paul Kappelmeier (*Ber.*, 1911, 44, 2718—2724).—Knorr, Rothe, and Averbeck's general results on the desmotropy of ethyl acetoacetate (this vol., i, 516) confirm those obtained by K. H. Meyer (this vol., i, 350), but these authors find that, in a state of equilibrium, the ester contains 2% of the enolic form, whilst Meyer's results indicated 7·71%.

The authors have therefore investigated the sources of error in Meyer's method, namely, the necessity of adding a slight excess of bromine before a recognisable yellow colour is obtained, the conversion of ketonic into enolic form during the titration, and the possible presence in the alcoholic bromine solution of substances which liberate iodine from potassium iodide (such are really present in old, but not in fresh, solutions); but when allowance is made for [illegible]

these errors, the proportion of the enolic form is still found to exceed 7%.

The principal errors may be eliminated by adding to the solution, immediately after the bromine, alcoholic β-naphthol solution, which does not react with iodine, but does so very rapidly with bromine, forming a product unacted on by hydrogen iodide; the solution of the ester in alcohol at $-7°$, and the addition of the alcoholic bromine and naphthol solutions need not occupy more than fifteen seconds. The bromide of the ethyl acetate is then estimated by addition of potassium iodide and titration of the separated iodine with thiosulphate. By this method the presence of 7·4% of the enolic form is indicated. The difference between this and Knorr, Rothe, and Averbeck's value hence remains unexplained.

This titration method can only be employed where the bromine is added instantaneously to the ester, and where the transformation of one form of the ester into the other is not too rapid.

The publication of Piccard's results (this vol., ii, 561) has led the author to apply the above method to the equilibrium of solutions of widely varying concentrations of ethyl acetoacetate in alcohol, benzene, carbon disulphide, and n-hexane. The surprising result was obtained that up to dilutions which can still be accurately investigated by the titration method, namely, $N/5$ – $N/10$, the proportion of the enolic form present continues to increase with the dilution, the equilibrium hence depending on the concentration. This is explained on the assumption that the solvent itself does not remain constant on dilution, but consists of a variable mixture of alcohol, etc., and the ester. Also, Dimroth (this vol., ii, 31) has shown that the equilibrium is dependent on the solubilities of the two components, and it may be that addition of the ester increases the solubility of the ketonic form and so increases its proportion.

For the four solvents named above, the curves connecting the logarithm of the concentration with the percentage of enolic compound in the ester apparently become perpendicular to the enolic axis at high dilutions, as though the equilibrium were then independent of the concentration, but the errors of the method are too great with dilute solution to permit of this relation being definitely established.

T. H. P.

Keto-enolic Tautomerism. IV. Ferric Chloride Reaction of Enols. KURT H. MEYER (*Ber.*, 1911, **44**, 2725—2729).—No quantitative measurements have been made of the velocity of enol-formation with ethyl acetoacetate, or of the quantity of enol-iron-compound formed with ferric chloride, but from their conductivity measurements Hantzsch and Desch (Abstr., 1902, i, 708) drew the conclusion that only very little enolate is present in an iron enolate solution of ethyl acetoacetate, in spite of the intensity of the colour. This conclusion is not confirmed by the author's results.

The estimation of enol in ethyl acetoacetate by titration with bromine (this vol., i, 350; preceding abstract) can be effected also in

presence of ferric chloride, the titration being conti[illegible] the violet colour of the enolate disappears. As the [illegible] returns again, owing to further enolisation, and can then [illegible] again by further addition of bromine water, and so on, [illegible] serves as a striking lecture experiment. In order to av[illegible] tion during the titration, this must be carried out [illegible] possible and at 0°.

Varying proportions of aqueous ethyl acetoacetate [illegible] chloride solution were mixed, left at 0° for an hour so tha[illegible] might be established, and titrated with $N/10$-bromine w[illegible] results show that the ferric chloride exerts a direct enolis[illegible] quantity of enol formed varying with, but not proporti[illegible] amount of ferric chloride added. The law of mass action [illegible] equation: $C_{enolate} = K.C_{enol}.C_{Fe} = K.C_{Fe}.C_{keto}/C_{H}$, the quantity [illegible] formed being dependent on the number of hydrogen [illegible] indeed, the complex salt can be decomposed and the solution [illegible] by addition of acid. With low concentrations of the ferri[illegible] its hydrolysis, and hence the free acid present in it, may be [illegible] so that it can be assumed that, in a state of equilibrium, the [illegible] ions correspond with the hydrochloric acid liberated fro[illegible] chloride by the enol. Hence $C_{enolate} = K\sqrt{C_{FeCl_3}.C_{keto}}$. The [illegible] this expression agree fairly well for low concentrations of [illegible] chloride, but vary considerably for the higher concentrations. [illegible] be that in the latter case the free acid in the ferric [illegible] influences the equilibrium, and that with higher enol c[illegible] which require larger amounts of bromine solution, the [illegible] hydrogen bromide destroys some of the enolate.

In alcoholic solution the quantity of enolate cannot be es[illegible] accurately, owing to the change of colour on titration b[illegible] distinct, but the colour of the enolate quickly re-appears, [illegible] velocity of conversion of keto- to enol-form is apparently cat[illegible] accelerated to a considerable extent.

That the slow formation of enolate is in reality due to the [illegible] ness of enolisation is shown by the fact that enolate forma[illegible] unimolecular reaction, its course being quite analogous with [illegible] enolisation by halogens (compare Lapworth, Trans., 1904, 85 [illegible] The velocity constant, $K = 0.017$ at 0°, shows that the catal[illegible] of ferric chloride is almost exactly as weak as that of free hydr[illegible] acid (this vol., i, 350). In alcoholic solution ferric chlorid[illegible] much more marked catalytic effect on enolisation. T. H. P.

Formation of Lævulic Acid from Glucosamine, Chit[illegible] Chitose. HEDWIG HAMBURGER (*Biochem. Zeitsch.*, 1911, 36, [illegible] —Lævulic and formic acids are produced when *d*-glucosamine [illegible] chitin are heated for four or five days with 25—30 per [illegible] sulphuric acid.

By treatment with sodium nitrite, glucosamine hydrochloride [illegible] be converted into chitose, and this when heated with hydrochl[illegible] also forms lævulic acid. These substances must therefore be in[illegible] in those groups contained in the protein molecule which yield læv[illegible] acid when hydrolysed with strong mineral acids. W. J. Y.

[illegible] Walden Inversion. VII. Optically Active Leucic ([illegible]hydroxyisohexoic) Acid and its Transformation into [illegible] hexoic Acid. HELMUTH SCHEIBLER and ALVIN S. WHEELER ([illegible] 44, 2684—2690. Compare Abstr., 1911, i).—The resolution of [illegible] hydroxyisohexoic acid into its optically active components [illegible] accomplished by the crystallisation of its quinidine salt. [illegible] on treatment with nitrous acid yields *l*-hydroxyisohexoic [illegible] the ethyl ester of which is converted by the action of bromine [illegible] into ethyl *d*-α-bromo*iso*hexoate. Since it has been [illegible] Fischer (Abstr., 1907, i, 194) that the *l*-bromo-ester may be [illegible] from the *l*-bromo-acid formed by the action of nitrosyl [illegible] *l*-leucine, it is, therefore, possible to convert the latter [illegible] ethyl ester of either *d*- or *l*-α-bromo*iso*hexoic acid.

[illegible] Hydroxy*iso*hexoic acid, prepared by the action of aqueous sodium [illegible] α-bromo*iso*hexoyl bromide, first at the ordinary temperature [illegible] then at 100°, crystallises in rhombic plates, m. p. 76—77° ([illegible] Rohmann, Abstr., 1908, i, 56; Gmelin, Abstr., 1893, i, [illegible]). The *ethyl* ester has b. p. 80—81°/16 mm., and yields *ethyl* [illegible]*hexoate*, b. p. 86—87°/11 mm., when treated with [illegible] and bromine.

[illegible] resolution of the acid into its optically active components may [illegible] effected by means of the quinine or brucine salts, but most readily [illegible] crystallisation of the quinidine salt.

[illegible] *hydroxyisohexoic acid* crystallises in thin prisms, m. p. 81—82°, [illegible] sintering at 78°, and has, in *N*-sodium hydroxide [illegible] 27·8° (±0·2°), in water $[\alpha]_D^{20}$ −10·4° (±0·2°). It may also be [illegible] by the action of nitrous acid on *l*-leucine, no appreciable [illegible] taking place during the transformation; the *barium* salt [illegible] analysed. The *d*-*isomeride* could not be obtained pure by the [illegible] of its alkaloidal salts, and is, therefore, best prepared [illegible] *d*-leucine and nitrous acid; in *N*-sodium hydroxide it has [illegible] (±0·2°).

[illegible] *hydroxyisohexoate*, prepared by esterifying the *l*-acid with [illegible] hydrogen chloride, has b. p. 79—80°/12 mm., $[\alpha]_D^{[illegible]}$ −11·07° [illegible] D [illegible] 0·965, and is converted by treatment with phosphorus [illegible] into ethyl *d*-α-bromo*iso*hexoate, considerable racemisation [illegible] accompanying the action.
F. B.

[illegible] Lactarinic Acid and Ketostearic Acid Isolated from Fungi [illegible] the genus Lactarius. J. BOUGAULT and C. CHARAUX (*Compt. [illegible]*, 1911, 153, 572—573*).—Thörner's lactarinic acid has been [illegible] from *Lactarius theiogalus*, *L. plumbeus*, etc., but does not occur [illegible] species. It is extracted by alcohol, and obtained as spangles, [illegible] 87°, having the composition $C_{18}H_{34}O_3$. The substance appears [illegible] a ketonic acid, since it yields an *oxime*, m. p. 59—61°, which [illegible] the Beckmann transformation, giving a *compound*, m. p. [illegible] the *ethyl* ester has m. p. 41°. Reduction of the acid by means [illegible] sodium and alcohol leads to the formation of an *hydroxy-acid*, [illegible] $H_{[illegible]}O_{[illegible]}$; this substance yields an *acetyl* derivative, m. p. 52—53°, [illegible] furnishes stearic acid when its iodo-derivative is reduced with zinc [illegible] acetic acid.
W. O. W.

* and *J. Pharm. Chim.*, 1911, [vii], 4, 337-343.

β-Butanolglycuronic Acid. SUMIO SANEYOSHI (*Biochem. Ze*[illegible] 1911, **36**, 22—24).—Methyl ethyl ketone when given [illegible] the mouth undergoes reduction in the body, and is [illegible] urine as a β-butanol derivative of glycuronic acid. [illegible] was isolated as the barium salt, $C_{10}H_{17}O_7Ba$, and from [illegible] did not reduce Fehling's solution directly, a gluco[illegible] attributed to it. [illegible]

Action of the Chlorides of Dibasic Fatty Acids on Ethyl Sodioacetoacetate. JOHANNES SCHEIBER [with P. [illegible] 1911, **44**, 2422—2429).—Chlorides of succinic, glutar[illegible] acids react with ethyl sodioacetoacetate to form comp[illegible] type $[CH_2]_n[CO\cdot CH(COMe)\cdot CO_2Et]_2$. In addition, su[illegible] reacts with 1 mol. of ethyl sodium acetoacetate, [illegible] *succinylacetoacetate*, $CO_2H\cdot CH_2\cdot CH_2\cdot CO\cdot CH(COMe)\cdot CO_2E$[illegible] sponding malonic ester derivative (Scheiber, Abstr., 190[illegible] has a cyclic structure, but the succinyl ester shows no tend[illegible] to form a γ-lactone or other cyclic derivative.

Ethyl succinylacetoacetate crystallises in prisms, m. p. [illegible] a red coloration with alcoholic ferric chloride. With phenylhy[illegible] four products are obtained :

(*a*) The *phenylhydrazine* salt of *ethyl-β-carboxypropion*[illegible] bis*phenylhydrazone*, m. p. 138°, forming colourless, unstable [illegible]

(*b*) A *pyrazole*, $C_{16}H_{18}O_4N_2$, the colourless crystals of [illegible] m. p. 43°.

(*c*) A *base*, $C_{14}H_{14}O_2N_2$ or $C_{28}H_{28}O_4N_4$, m. p. 157°.

(*d*) A *product*, m. p. 214—215°, soluble in alcohol.

With hydroxylamine an iso*oxazole*, m. p. 81°, is obtained. [illegible] hydrazine the products are a *hydrazone*, m. p. 188°, and a [illegible] m. p. 118°.

Ethyl succinyldiacetoacetate was obtained as an oil; it [illegible] cornflower-blue coloration with sulphuric acid changing to gre[illegible]

Ethyl glutaryldiacetoacetate, $CH_2[CH_2\cdot CO\cdot CH(COMe)\cdot CO_2E$[illegible] oil of acid properties; with phenylhydrazine it gives *glutar*[illegible] bis-*phenylhydrazide*, $CH_2[CH_2\cdot CO\cdot NH\cdot NHPh]_2$, which crystallises [illegible] plates, m. p. 217—218°.

Ethyl adipyldiacetoacetate is also an oil; with phenylhydrazine *adipic acid*-bis-*phenylhydrazide*, $C_2H_4(CH_2\cdot CO\cdot NH\cdot NHPh)_2$ [illegible] it crystallises in nacreous, lustrous plates, m. p. 206—207°. E. F. A.

Preparation of Additive Compounds of Chloral with Amides. CHEMISCHE FABRIK GEDEON RICHTER (D.R.-P. 2[illegible]).—When chloral is fused with a molecular proportion of an acid amide an additive compound is produced.

Bromoisovaleramide-chloral, $CHMe_2\cdot CHBr\cdot CO\cdot NH_2,CCl_3\cdot CHO$, forms small, colourless, odourless crystals with an intensely bitter taste and m. p. 116—118° (decomp.); it is insoluble in petroleum and in water, but dissolves readily in other organic solvents, and is of therapeutic value. F. M. G. M.

Hexose Phosphoric Acid Ester. A. von Lebedeff (*Biochem.* [illegible] 1911, **36**, 248—260. Compare Abstr., 1910, i, 716; Young, [illegible]). The author gives a short historical sketch of the rôle of [illegible] acid in alcoholic fermentation. A further investigation of [illegible] and *p*-bromophenyl-hydrazones showed that the derivatives [illegible] molecule of hexose to two molecules of phosphoric acid, [illegible] with Young's suggested formula for the phosphoric [illegible] $C_6H_{10}O_4(RPO_4)_2$. The sodium and lead salts of the osazone of [illegible] were prepared and analysed, the full experimental method [illegible] and the formulæ given by the author two years ago [illegible]. The author claims that the possibility of ascribing [illegible] formula given by Young is due to his own investigations, [illegible] by him of osazones and hydrazones. The paper is [illegible] versial. S. B. S.

Preparation of Phosphoric Acid Esters of Carbohydrates and Glycerol. Carl Neuberg and E. Kretschmer (*Biochem. Zeitsch.*, [illegible] **36**, 5—14). *Calcium* d-*galactophosphate*, $C_6H_{11}O_9PCa,H_2O$, is [illegible] by slowly adding a solution of phosphoryl chloride in [illegible] to a suspension of calcium carbonate in water containing [illegible], which is stirred continuously and cooled in a freezing [illegible]. It is a white powder, which in solution in water reduces [illegible] solution and is fermented by beer-yeast.

[illegible], when treated in the same manner, gave a product which con[illegible] a double salt of *calcium laevulosephosphate* and calcium chloride, [illegible] which the latter could not be removed. The compound was obtained, [illegible] by partly hydrolysing calcium sucrose-phosphate by heating [illegible] fifteen minutes with dilute hydrochloric acid. It is a white [illegible], which gives Seliwanoff's reaction for lævulose, reduces [illegible] solution, and is readily fermented by yeast, thus differing [illegible] calcium dextrose-phosphate and sucrose-phosphate. It has the [illegible] $C_6H_{11}O_9PCa,H_2O$.

Calcium glycerolphosphate was obtained in a similar manner to the [illegible] phosphate. W. J. Y.

Nature of the So-called Gallisin in Commercial Starch-syrup. Jos. Gatterbauer (*Zeitsch. Nahr. Genussm.*, 1911, **22**, [illegible]). That portion of commercial starch syrup which ferments [illegible] difficulty and to which the name gallisin has been applied [illegible] of a new carbohydrate, together with a small quantity of [illegible]; dextrins are not present. This carbohydrate is termed *glucosin* provisionally, and is an isomeride of maltose, yielding only [illegible] on hydrolysis. It may be separated from fermented starch-syrup as a viscous syrup, which, by treatment with a mixture of [illegible] alcohol and ether, is converted into a white or yellowish-white powder. Beer-yeast ferments glucosin slowly, whilst yeast-[illegible] and emulsin convert it into dextrose. Mineral acids and [illegible] acid also convert glucosin into dextrose, but with high concentrations of mineral acids the reaction is reversible. The *phenyl-osazone*, m. p. 97—100°, is soluble in hot water and in alcohol; the *p-nitrophenylosazone*, m. p. 240°, is a red powder, which yields a

blue coloration when treated with sodium hydroxide. G... yields amorphous esters with benzoyl chloride, *p*-chlorob... *m*-nitrobenzoyl chloride, and benzenesulphonyl chlorid... formed by the action of acids on dextrose in the manufa... syrup (compare Abstr., 1905, i, 684).

W. P.

Viscosity of Cellulose Solutions. HERMANN ... (*Zeitsch. angew. Chem.*, 1911, **24**, 1892—1896).—A number of determinations of the viscosity of cuprammonium solutions of various ... cellulose, such as cotton, wood-pulp, cotton-wool, filter paper ... have led the author to the conclusion that these viscosity ... tions supply useful information on the nature and tech... celluloses.

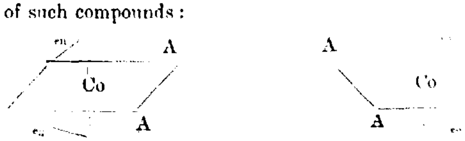
The cuprammonium solution employed was prepared by ... solution containing 59 grams of copper sulphate with ... hydroxide and dissolving the basic copper sulphate th... ammonium hydroxide (D 0·900) to form one litre of ... quantity of cellulose was dissolved in this solution in ... to give a solution containing one gram of the anhydro... 50 c.c. The viscosity was determined by means of a spe... Ostwald's capillary viscometer.

It is found that previous treatment of the cellulose with ... agents produces a marked decrease in the viscosity of ... ammonium cellulose solution; the same result is brought ... by heating the cellulose for about fifteen hours at 120—125 ... other hand, treatment of the cellulose with a cold 5 ... sodium hydroxide for about twenty-four hours, or with a ... solution for one hour, does not affect the viscosity of the ... from which observation the conclusion is drawn that cotton ... undergo a chemical change during mercerisation. Sodium hydr... however, does act on cotton chemically, although very ... cotton which has been soaked in a 20% solution of sodium ... pressed, and kept in a stoppered bottle for several months, ... very readily in a cuprammonium solution and forms a solution ... a low viscosity.

Cuprammonium solutions of hydrocellulose, obtained by the ... of dilute mineral acids on cellulose, are far less viscid than ... solutions of cellulose which have been acted on by bleaching ...

W. H ...

The Asymmetric Cobalt Atom. II. ALFRED WERNER (... 1911, **44**, 2445—2455).—The author finds that compounds ... complex radicles $[A_2\,Co\,en_2]$, in which the two groups A are ... *cis*-position with respect to each other, can be resolved into ... optically active isomerides, which is in accordance with the ... formulæ of such compounds:



[illegible] case is quite different from that reported in the previous [illegible] (this vol., i, 613). Compounds of the type $\left[\begin{matrix}A\\B\end{matrix}\text{Co en}_2\right]$ [illegible] tetrahedra, with four different groups (Co, A, B, and en), [illegible] mirror images of each other, since the ethylenediamine [illegible] different orientation in space in the two tetrahedra, [illegible] in the same plane as A, and the other in the same [illegible] This is no longer the case with compounds of the type [illegible] that they cannot be said to contain an asymmetric [illegible] the image and mirror image do not contain a plane [illegible] there occurs a kind of molecular asymmetry which [illegible] notes as *Molecular Asymmetry I.* It is of a simpler [illegible] that occurring with carbon compounds, since there are [illegible] groups, ethylenediamine and A, attached to the cobalt atom. [illegible] which have been resolved belong to the 1 : 2-dinitro-[illegible]amine series (the flavo-series), $\left[\begin{matrix}(1)\ O_2N\\(2)\ O_2N\end{matrix}\text{Co en}_2\right]$, and in [illegible] their resolution, interesting analogies have been found [illegible] compounds. When *d*-camphorsulphonic acid is used, the [illegible] dinitrodiethylenediamine cobalt radicle is difficultly [illegible] that of the *d* radicle is easily soluble. When *d*-bromo-[illegible] acid is used, the least soluble salt is that formed [illegible] radicle. These relations are just the reverse of those [illegible] in the resolution of optically active carbon compounds, [illegible], in the resolution of tetrahydroquinaldine.

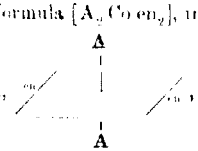
[illegible] 1 : 2-dinitrodiethylenediaminecobalti-salts show a very [illegible] anomalous rotation dispersion, the *D* line being strongly [illegible] whereas the *C* line is rotated to a very small extent or not [illegible] solutions the following rotations were observed :

$[a]$	$[M]$		$[a]$	$[M]$
[illegible]	±153	Bromide	[illegible] 12·5 / 11·9	±157
[illegible]	±139	Nitrate	[illegible] 11·5 / 11·5	±136
[illegible] / −29·5	±111	Sulphate	[illegible] 45 / 45	±143
[illegible] 66	[illegible] 383·5	*l*-Flavo-*l*-camphor-sulphonate	16	[illegible] 80·32

[illegible] great differences exist in the solubilities of the active and [illegible] salts, as shown by the following table, where the solubilities [illegible] in terms of grams of salt in 100 c.c. of water :

	Temperature.	*d*-Isomeride.	*l*-Isomeride.	Racemate.	1 : 6-Dinitro-salts.
[illegible]	22°	4·36	4·17	1·2	2·202
[illegible]	22	0·49	0·46	0·56	2·652
[illegible]	28	1·63	1·71	2·55	—

[illegible] of the formula $[A_2\text{Co en}_2]$, in which the A-radicles are [illegible] *trans*-position,



should not show optical

isomerism, and in proof of this it was not found possible to [illegible] salts of the 1 : 6-dinitrodiethylenediaminecobalti-series [illegible]

The cases of isomerism which have been proved to [illegible] diacido-diethylenediaminecobalti-salts may be summari[illegible]

(1) *Cis-trans*-isomerism :

$$\left[\begin{matrix}(1)\ O_2N\\(2)\ O_2N\end{matrix}\ Co\,en_2\right]X \quad \text{and} \quad \left[\begin{matrix}(1)\ O_2N\\(6)\ O_2N\end{matrix}\ Co\,en_2\right]X.$$

Flavo-salts. Croceo-salts.

(2) Salt isomerism :

$$\left[\begin{matrix}(1)\ ON{\cdot}O\\(2)\ ON{\cdot}O\end{matrix}\ Co\,en_2\right]X \quad \text{and} \quad \left[\begin{matrix}(1)\ O_2N\\(2)\ O_2N\end{matrix}\ Co\,en_2\right]X.$$

1 : 2-Dinitritodiethylenediaminecobalt salts. Flavo-salts.

and also the 1 : 6-dinitritodiethylenediaminecobalt [illegible] croceo salts.

(3) Ionisation metamerism :

$$\left[\begin{matrix}O_2N\\O_2N\end{matrix}\ Co\,en_2\right]X \quad \text{and} \quad \left[\begin{matrix}O_2N\\X\end{matrix}\ Co\,en_2\right]NO_2.$$

X can be either Cl, Br, or SCN, etc.

(4) Co-ordination polymerism :

$$\left[\begin{matrix}O_2N\\O_2N\end{matrix}\ Co\,en_2\right]_3\left[Co(NO_2)_6\right] \quad \text{and} \quad \left[Co\,en_3\right]\left[Co(NO_2)_6\right].$$

(5) Mirror image isomerism :

$$d\text{- and } l\text{-}\left[\begin{matrix}(1)O_2N\\(2)O_2N\end{matrix}\ Co\,en_2\right]X.$$

The inactive 1 : 2-dinitrodiethylenediaminecobalt salts [illegible] Abstr., 1901, i, 511) are best obtained by heating together [illegible] of potassium cobaltinitrite and 48 grams of 10% ethylenediamine [illegible] the mixture begins to froth. The dark brown solution is [illegible] from unchanged cobaltinitrite, and on keeping deposits [illegible] yellow crystals of the 1 : 2-dinitronitrite. The mother [illegible] evaporating, gives at first a further quantity of the salt, and [illegible] mixture of the 1 : 2- and 1 : 6-dinitro-salts which can be separated [illegible] fractional crystallisation. The iodide is obtained by [illegible] hot solution with sodium iodide.

In the resolution of the iodide by means of silver *d*-[illegible] sulphonate, a precipitate of a mixture of silver iodide and [illegible] nitrodiethylenediaminecobalt *d*-camphorsulphonate is first [illegible] from the hot solution, from which mixture the camphorsulph[illegible] may be extracted with hot water. The mother liquor from [illegible] mixture deposits a partial racemate on cooling, from which [illegible] quantities of the *l*-salt can be obtained by appropriate [illegible] (recrystallisation, etc.). When about 20 grams of the *l*-salt have [illegible] obtained, the mother liquors are united, the iodide [illegible] and then treated with silver *d*-bromocamphorsulphonate. After collecting the silver iodide, the hot solution, on cooling, deposits brown needles of *d*-dinitrodiethylenediaminecobalt *d*-bromocamphor-sulphonate.

To prepare the various active salts, the camphor- and bromo-camphorsulphonates were precipitated with excess of sodium iodide, the aqueous suspension of the iodide transformed into the base by shaking with silver oxide, and the salts then obtained by neutralisation of the base with the respective acids.

d- and l-*Dinitrodiethylenediaminecobalt chlorides*, YCl, where Y = $\left[\begin{matrix}O_2N\\O_2N\end{matrix}Co\,en_2\right]$, form brownish-yellow, columnar crystals. The ... deep brown in colour, and crystallises in broad, thick ... The *bromides*, YBr, are similar in colour and shape to the ... The *active iodides*, YI, give well-developed octahedral ..., whereas the inactive salt is microcrystalline and of prismatic ... The active *nitrates*, YNO_3, form stout, prismatic or columnar ... distinguished from the long prisms of the inactive compound. The active *sulphates*, Y_2SO_4, give flat prisms or tablets, whilst the inactive salt forms long, silky, light yellow crystals. The *active* ...ates, $YClO_4$, crystallise in aggregates of short, stout prisms ..., whilst the *inactive* salt gives rhombic leaflets of amber-... colour.

... 2-*Dinitrodiethylenediaminecobalt* d-*camphorsulphonate*,

$$Y(O_3S\cdot C_{10}H_{15}O),$$

... long, flat, pointed, golden-yellow crystals. d-1:2-*Dinitrodiethylenediaminecobalt* d-*bromocamphorsulphonate*, $Y(O_3S\cdot C_{10}H_{14}OBr)$, ... flat, centimetre-long, brownish-yellow prisms. 1:6-*Dinitrodiethylenediaminecobalt* d-*camphorsulphonate*,

$$\left[\begin{matrix}(1)\,O_2N\\(6)\,O_2N\end{matrix}Co\,en_2\right][O_3S\cdot C_{10}H_{15}O],$$

... stout, amber-yellow or brownish-yellow prisms, which are often ... centimetre long; $[M]_D + 45\cdot2 - 47\cdot7°$. T. S. P.

Preparation of Mercury Derivatives of Alkali Alkyldithiocarbamic Acetates. Les Établissements Poulenc Frères and ... Fourneau (D.R.-P. 235356. Compare Abstr., 1907, i, 594).—... *dithiocarbaminoacetate*,

$$CO_2Et\cdot CH_2\cdot NMe\cdot CS\cdot S\cdot NH_2Me\cdot CH_2\cdot CO_2Et,$$

..., m. p. 70—71°, is prepared by slowly treating a cooled solution of ...methylaminoacetate, $CO_2Et\cdot CH_2\cdot NHMe$ (60 parts), in anhydrous ... with carbon disulphide (25 parts) in the same solvent. An energetic reaction takes place; an oil separates which rapidly solidifies, ... is purified by crystallisation from ether or acetone. The *mercury* ..., $(CO_2Et\cdot CH_2\cdot NMe\cdot CS\cdot S)_2Hg$, a pale yellow powder, is obtained ... the foregoing compound is treated with a saturated solution ... mercuric chloride, and this, when slowly treated with a 30% solution of sodium hydroxide (containing 2 mols. NaOH), yields a ..., yellow precipitate of the *mercury sodium* double salt,

$$(CO_2Na\cdot CH_2\cdot NMe\cdot CS\cdot S)_2Hg,$$

which is isolated in the form of a yellow powder. If the solution of the mercury sodium salt be heated until it darkens, a *compound*, $CO_2Na\cdot CH_2\cdot NMe\cdot CS\cdot S\cdot Hg\cdot S\cdot CH_2\cdot CO_2Na$, is obtained as a green powder. F. M. G. M.

Preparation of Optically Active Polypeptides from Racemic Compounds. EMIL ABDERHALDEN and HEINRICH [illegible] (*Zeitsch. physiol. Chem.*, 1911, **74**, 394—408).—As a general [illegible] ferments only hydrolyse those polypeptides which [illegible] amino-acids which occur naturally. An exception [illegible] *d*-leucyl-*l*-tryptophan, which, according to Hans Fischer [illegible] i, 22, 599), is hydrolysed by the liver and by pancreatic [illegible] and Schuler (Abstr., 1910, i, 304) have pointed out [illegible] racemisation in the preparation of an optically active [illegible] consider the hydrolysis observed by Fischer to be [illegible] *l*-tryptophan. The action of pressed yeast juice towards *dl*-leucyl-*l*-tryptophan indicates that only *l*-leucyl [illegible] hydrolysed by the enzyme; the racemic compound [illegible] of *l*-leucine, *l*-tryptophan, and *d*-leucyltryptophan; *d*-leucyl [illegible] when pure is not attacked.

It is possible by means of enzymes to obtain optically active peptides from racemic compounds; these are the [illegible] natural compounds, but a comparison of the magnitude [illegible] power is possible.

Prepared by the action of yeast juice in [illegible] *d*-leucylglycine has $[\alpha]_D^{20}$ $-87.87°$ to $-88.5°$, and [illegible] $[\alpha]_D^{20}$ $+37.62°$ to $+37.1°$, in both cases somewhat higher [illegible] those obtained by Fischer for the optical antipodes.

Remarks on Henze's Paper on the History of Iodo [illegible] Acid. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **74**, [illegible] Compare this vol., i, 617).—Certain misstatements [illegible] Henze's paper are corrected.

W. [illegible]

Methylated Guanidines. MARTIN SCHENCK (*Arch. Pharm.*, 1911, **249**, 463—480. Compare Abstr., 1910, i, 99, 545, [illegible] part of this paper describes attempts to prepare *a*-methylguanidine, $NMe:C(NH_2)_2$, the second, efforts to obtain *aβ*-dimethylguanidine, $NMe:C(NH_2)\cdot NHMe$, and the third gives an account of the [illegible] of some new methylated guanidines and substances related to [illegible] failure to obtain *a*-methyl- and *aβ*-dimethyl-guanidines is [illegible] tendency these substances have to transform immediately into [illegible] and *s*-dimethyl-guanidines respectively.

By the interaction of thiocarbamide and methylamine in presence of mercuric oxide, *β*-methylguanidine and dicyanodiamide are [illegible] first probably by the action of cyanamide, first formed on [illegible] Ethyl iminocarbonate furnishes with methylamine, [illegible] guanidine; with dimethylamine, *as*-dimethylthiocarbamide [illegible] $B_2,HAuCl_4$, m. p. 105°; platinichloride, $B_2,H_2PtCl_6,2H_2O$ [illegible] anhydrous), and with ammonia, guanidine. Ethyl [illegible] appears to undergo methylation when left fourteen days [illegible] with methyl iodide and potassium hydroxide solution, since the product reacts with methylamine to form *aββ'*-trimethylguanidine, with [illegible] methylamine to form a substance giving a crystalline aurichloride, $C_{15}H_{30}O_2N_{10}Au_2Cl_8$, m. p. 250—252°, and with ammonia in [illegible] form *β*-methylguanidine (?). With ammonia in one case a [illegible]

[illegible] guanidine was obtained, indicating the presence of un[illegible] ester in the material used. Ethyl methyliminodithiocar[illegible] $NMe:C(SMe)_2$, gives with methylamine in alcohol, $\alpha\beta\beta'$-tri[illegible]guanidine, with ammonia in alcohol, β-methylguanidine, and [illegible]ethylamine a substance yielding a crystalline aurichloride, [illegible] below 100°.

[illegible] preparation of $\alpha\beta$-dimethylguanidine, $NMe:C(NHMe)\cdot NH_2$, [illegible] methods were tried unsuccessfully: Dimethylthiocarb[illegible] treated with ammonia in alcohol in presence of mercuric oxide [illegible] $\alpha\beta\beta'$-trimethylguanidine with some $\beta\beta'$-dimethylguanidine [illegible] Chanel, Abstr., 1893, i, 297). *Dimethylethyl-ψ-thiocarbamide*, [illegible] $NHMe\cdot SEt$, in the form of its *ethiodide*, m. p. 100° (approx.), [illegible] ammonia in alcohol $\beta\beta'$-dimethylguanidine (compare Noah, [illegible], 1241), and the same substance was obtained by the action [illegible] on $\alpha\beta\beta'$-trimethyl-ψ-thiocarbamide.

[illegible]*methylguanidine aurichloride*, $NH:C(NHMe)\cdot NMe_2,HAuCl_4$, [illegible] obtained by the addition of gold chloride to the product [illegible] from the interaction of methylthiocarbamide methiodide [illegible] 156°) and dimethylamine in alcohol, forms small needles, [illegible] easily soluble in water.

[illegible]*methylthiocarbamide methiodide*, m. p. 210—212°, obtained by [illegible] combination of its two components in alcohol, gives an *auri*[illegible], $(S:NHMe)_2,CH_3Cl,AuCl_3$, m. p. 122° (approx.), on treatment [illegible] silver chloride and then with gold chloride. The similarly [illegible] *platinichloride* has m. p. 192—194°. The methiodide reacts [illegible]methylamine in alcohol to form $\alpha\beta\beta'$-trimethylguanidine, which is [illegible] obtained by the action of methylamine on the corresponding [illegible]. The free trimethyl-ψ-thiocarbamide regenerated from the [illegible] gives with ammonia in alcohol, as stated above, $\beta\beta'$-di[illegible]guanidine, and with dimethylamine, $\alpha\beta\beta\beta'$-tetramethylguanidine, [illegible] the *aurichloride* has m.p. 117° (approx.). T. A. H.

Melamazine from Hydrazine Salt and Dicyanodiamide. [illegible] A. Hofmann and Oskar Ehrhart (*Ber.*, 1911, **44**, [illegible]717).—Aminoguanidine nitrate may be easily and cheaply [illegible] from "Nitrolime" (50% calcium cyanamide) and hydrazine [illegible].

When heated with hydrazine or one of its salts, dicyanodiamide [illegible]guanidine) yields a series of hydrazine derivatives, among them [illegible], $(C_3N_3NH_2)_2(NH\cdot NH)_2,H_2O$, distinguished by its ability [illegible] up oxygen in alkaline solution, giving an intensely bluish-violet [illegible] matter. The *hydrochloride*, $C_6H_8N_{12},HCl$, dissolves in hot [illegible], giving a colloidal solution. The azine exhibits only slight [illegible] capacity, as water effects partial hydrolysis and ammonia [illegible] the base. It is very stable towards strong acids; when [illegible] with fuming hydrochloric acid for twenty-four hours at 170°, [illegible] largely converted into carbon dioxide, ammonium chloride, and [illegible] hydrochloride, whilst with fuming sulphuric acid at 190° [illegible] slowly decomposed, giving principally ammelide (melanurenic [illegible]. Nitro-hydrochloric acid also attacks it slowly, giving ammeline [illegible]. With excess of alkaline permanganate solution, it yields four

atoms of nitrogen per molecule, and, if the reaction is carried to an end on the water-bath, the hydrazine groups are burnt away, whilst the cyanamide part of the molecule loses part of its ammonia and yields substances of the ammeline-ammelide group.

The bluish-violet coloration formed when an alkaline [illegible] the azine is left exposed to the air is visible even after [illegible] 100,000 parts of water. Reducing agents, such as [illegible] hydrazine, hyposulphite, and zinc dust, decolorise the [illegible] but the colour soon returns in the air. On acidification [illegible] alkaline solution becomes wine-red and then colourless, [illegible] of transparent, flocculent matter.

The colouring matter can be fixed on unmordanted [illegible] soaking the tissue with the alkaline solution and then [illegible] chloride solution; the violet colour is changed to red by [illegible] by acetic acid. The colouring matter was isolated as [illegible] $(C_6HO_2N_{10})_2Ba$, in the form of an opaque, violet-black [illegible] bronzy lustre; the *thallium* salt, $(C_6O_2N_{10})Tl_2H$, was also prepared.

In concentrated sulphuric acid melamazine gives with [illegible] nitrate an intense yellowish-red coloration, which [illegible] brucine reaction, and on warming turns to blue and then [illegible] with evolution of gas. Hydrogen peroxide in concentrated [illegible] acid also gives a transitory reddish-yellow coloration, whilst [illegible] acid yields a deep reddish-brown colour, changing to [illegible] evolution of gas, on heating. [illegible]

Prussian Blue and Turnbull's Blue. III. Erich M[illegible] [and, in part, G. Wegelin, Frederick P. Treadwell, [illegible] Diefenthaler] (*J. pr. Chem.*, 1911, [ii], **84**, 353—369. Compare [illegible], 1909, i, 142, 705). —The composition of the precipitates [illegible] mixing (0·1 molar) solutions of hydroferrocyanic acid and ferric chloride and of hydroferricyanic acid and ferrous chloride [illegible] investigated by methods similar to those already described. [illegible] experiments on the composition of the precipitates formed [illegible] potassium ferrocyanide and ferric chloride and from potassium ferricyanide and ferrous chloride have been repeated, with results [illegible] somewhat from those previously given.

The precipitates obtained by mixing potassium ferrocyanide [illegible] ferric chloride consist of $Fe_4'''[Fe(CN)_6]_3''''$ only when the [illegible] $K_4[Fe(CN)_6]/FeCl_3(=x)<0·75$. When x lies between 0·75 and [illegible] the precipitate consists of a mixture of $Fe_4'''[Fe(CN)_6]_3''''$ and $KFe'''[Fe(CN)_6]''''$, whilst as x becomes greater than 0·[illegible] a mixture of these compounds with gradually increasing amounts of $K_2Fe''[Fe(CN)_6]''''$ is produced.

With hydroferrocyanic acid and ferric chloride, when the ratio $H_4[Fe(CN)_6]''''/FeCl_3(=y)<0·75$, the precipitate has the composition $Fe_4'''[Fe(CN)_6]_3''''$. For values of y between 0·75 and 0·85 the precipitate consists of the latter compound mixed with $HFe'''[Fe(CN)_6]''''$. When $y>0·85$ the precipitate consists of a mixture of these compounds with $Fe_2''[Fe(CN)_6]''''$.

In the case of potassium ferricyanide and ferrous chloride, when the ratio $H_3[Fe(CN)_6]'''/FeCl_2(=z)<0·714$, $KFe_2''Fe_5'''[Fe(CN)_6]$[illegible]

[illegible] For values of z lying between 0·714 and 0·75, this is [illegible] by $KFe''Fe_3''[Fe(CN)_6]_3''''$. When z varies from 0·75 to [illegible] the precipitate consists of a mixture of $KFeFe_3''[Fe(CN)_6]_3''''$ [illegible] $Fe(CN)_6]''''$, whilst for values of $z > 0·9$, the two latter com[illegible] accompanied by $Fe_4''[Fe(CN)_6]''''$, produced according to [illegible] $4KFe''[Fe(CN)_6]'''' = Fe_4''[Fe(CN)_6]'''' + K_4[Fe(CN)_6]''''$. [illegible] results were obtained in the case of ferrous chloride and [illegible] acid. When the ratio $H_4[Fe(CN)_6]$: $FeCl_2 < 0·75$, [illegible] consists of a mixture of $HFe_2''Fe''[Fe(CN)_6]_3$ and [illegible] $Fe(CN)_6$; if the ratio $> 0·78$, a mixture of the latter [illegible] with $HFe''[Fe(CN)_6]''''$ and $Fe_4''[Fe(CN)_6]$ is produced.

F. B.

[illegible] of Hydrazine. VI. Reaction between Mercuric [illegible] and Hydrazine Hydrate in Alcoholic Solution. C. F. [illegible] V. E. NUNEZ (*J. Amer. Chem. Soc.*, 1911, 33, 1555—1563).—[illegible] Shetterly (Abstr., 1909, ii, 658) have shown that when an [illegible] of hydrazine sulphate is heated with either yellow or [illegible] oxide, neither ammonia nor azoimide is produced, but that [illegible] oxide is added gradually to a slightly alkaline solution of [illegible], both ammonia and azoimide are formed in appreciable [illegible].

[illegible] has now been made of the action of mercuric oxide on [illegible] solution of hydrazine hydrate, and it has been found that [illegible] ordinary temperature the reaction proceeds in accordance with [illegible] $N_2H_4,H_2O + 2HgO = N_2 + 2Hg + 3H_2O$. The amount of [illegible] actually obtained was slightly less than that required by [illegible]. Neither ammonia nor azoimide was produced, but [illegible] were obtained of the formation of ethylideneazine. [illegible] diethyl was also found to be a product of the reaction, [illegible] with a white, waxy, solid compound containing carbon, [illegible], and about 55% of mercury. The latter substance has [illegible] odour, resembling that of garlic, does not show a definite [illegible] and when applied to the skin produces painful and slow-healing [illegible]. The same compound is slowly produced by the action of [illegible] daylight on mercury diethyl.

E. G.

[illegible] Constitution of Aliphatic Diazo-compounds and of [illegible]. JOHANNES THIELE (*Ber.*, 1911, 44, 2522—2525).—A [illegible] paper in which arguments are brought forward in favour of [illegible] formula for certain products of the action of hydrazine on [illegible] and of the formula HN:N:N for azoimide.

H. W.

[illegible]alkylsilicanes. ARTUR BYGDÉN (*Ber.*, 1911, 44, 2640—2652). [illegible] examination of the action of magnesium alkyl halides on [illegible] chloride shows that the *mono*-alkyl derivatives, $SiRCl_3$ [illegible] ethyl, propyl, butyl, *iso*butyl, or *iso*amyl), and tetra-alkyl[illegible] are obtained with comparative ease, but the separation of the [illegible] and trialkyl derivatives presents great difficulties, and these [illegible] have not been obtained pure. Magnesium methyl bromide [illegible] more efficient reagent than the iodide, and by its means tetra[illegible]silicane, b. p. 26—27°, is easily obtained.

The following substances have been prepared by the usual Grignard reaction; the desired product is finally separated from its ethereal solution by treatment with concentrated sulphuric acid, in which the ether (and usually a small quantity of unexamined silicon derivatives) dissolves, leaving the desired product, which is removed by distillation. *Trimethylpropylsilicane*, $SiMe_3Pr$, b. p. 89·5° (corr.), D_4^{15} 0·7063, from trichloropropylsilicane and magnesium methyl bromide (3·3 mols.); *dimethyldiethylsilicane*, $SiMe_2Et_2$, b. p. 95·8° (corr.), D_4^{15} 0·7214, from dichlorodiethylsilicane and magnesium methyl iodide (2·5 mols.); *trimethylbutylsilicane*, b. p. 115·1° (corr.), D_4^{15} 0·7227, from trichlorobutylsilicane and magnesium methyl bromide (3·2 mols.); *dimethylethylpropylsilicane*, b. p. 121·0° (corr.), D_4^{15} 0·7347, from dichloroethylpropylsilicane and magnesium methyl bromide (2·3 mols.); *trimethylisoamylsilicane*, b. p. 131·5° (corr.), D_4^{15} 0·7322, from trichloroisoamylsilicane and magnesium methyl bromide (3·2 mols.); *dimethylethylisobutylsilicane*, b. p. 138·0° (corr.), D_4^{15} 0·7463, from dichloroethylisobutylsilicane and magnesium methyl bromide (2·3 mols.).

Tetra-ethylsilicane has b. p. 153·0° (corr.), and D_4^{15} 0·7694.

The preceding tetra-alkylsilicanes have an odour of petroleum, are almost unattacked by concentrated sulphuric acid or alkalis, are oxidised by concentrated nitric acid at a high temperature, react with chlorine in the cold and with bromine by warming, and explode when their mixture with air or oxygen is heated. The b. p. is lower and the molecular volume (of isomerides) is greater, the larger is the number of methyl groups directly attached to the silicon atom.

The new chlorosilicanes required in the preceding syntheses are *trichlorobutylsilicane*, $C_4H_9{\cdot}SiCl_3$, b. p. 148·5—149·5°, D_4^{15} 1·169, from magnesium butyl bromide and silicon tetrachloride; *trichloroisobutylsilicane*, b. p. 138—143°, D_4^{15} 1·161, prepared like the preceding compound; *dichloroethylpropylsilicane*, b. p. 152—158°, D_4^{15} 1·048, from trichloropropylsilicane and magnesium ethyl bromide; *dichloroethylisobutylsilicane*, b. p. 165—174°, from trichloroisobutylsilicane and magnesium ethyl bromide. C. S.

Organo-metallic Ester Compounds. I. Iodostanni-ester Compounds. BRUNO EMMERT and WILHELM ELLER (*Ber.*, 1911, 44, 2328—2330).—Tin reacts with ethyl iodoacetate in presence of iodine to form ethyl di-iodostanni-diacetate, $SnI_2(CH_2{\cdot}CO_2Et)_2$. Compounds of this type differ from the alkyl compounds of the metals in being completely decomposed by water and alkalis, thus:

$$SnI_2(CH_2{\cdot}CO_2Et)_2 + 2H_2O = 2CH_3{\cdot}CO_2Et + SnO_2 + 2HI.$$

They appear to yield salts when treated with silver nitrate or sulphate, but so far these have not been separated from their decomposition products. Treated with the Grignard reagent they give the corresponding tin tetra-alkyls.

Ethyl di-iodostanni-diacetate, m. p. 101·5° (corr.), crystallises from carbon tetrachloride on addition of ether in colourless, odourless needles. It is decomposed by baryta into ethyl acetate, stannic oxide, and hydriodic acid. With magnesium phenyl bromide and magnesium ethyl bromide, it gives tin tetraphenyl and tin tetraethyl respectively.

Ethyl di-iodostanni-di-o-benzoate, obtained by heating ethyl o-iodo

...nate (5 grams), tin foil (1·2 grams), and a little iodine, in a closed ...be during five days at 150°, crystallises in greyish-yellow, microscopic ...dles, and is practically insoluble in all solvents. T. A. H.

$\Delta^{1:3}$-Dihydrobenzene [$\Delta^{1:3}$-*cyclo*Hexadiene]. NICOLAI ZELINSKY ...d ALEXANDER GORSKY (*Ber.*, 1911, 44, 2312—2316*).—Doubts have ...en expressed by Brühl (Abstr., 1908, ii, 1002) and by Harries and ...e Splawa-Neyman (Abstr., 1909, i, 218) as to the accuracy of the ...ta published by the authors regarding $\Delta^{1:3}$-*cyclo*hexadiene (Abstr., ...908, i, 619, 732), the latter suggesting that the apparent absence of ...tical exaltation in this hydrocarbon, in spite of the presence of con...gated double linkings, was due to the occurrence of *cyclo*hexene in ...e material examined. The authors find that when quinoline reacts ...ith 1:2-dibromo*cyclo*hexane, the products obtained depend on the ...lative quantities used and the method of mixing. When the dibromo-...rivative is added drop by drop to quinoline in excess, the product is a ...ixture of *cyclo*hexadiene and *cyclo*hexene, but the material they ...riginally worked with could not have contained more than a trace of ...*clo*hexene. Further, determinations of the molecular refractions of ...ixtures of $\Delta^{1:3}$-dihydro-*m*-xylene (Klages, Abstr., 1907, i, 597) with ...3-dimethyl*cyclo*hexene (Abstr., 1902, i, 2) show that the latter does ...ot mask the optical exaltation of the former to any considerable extent. ...Moreover, the ultra-violet absorption spectra of the two *cyclo*hexadienes ...xamined by the authors (*loc. cit.*) are normal and similar, indicating ...hat the hydrocarbon now under discussion is homogeneous.

Bromo-Δ^1-cyclo*hexene*, b. p. 164—166°, or 69°/35 mm., D_4^{20} 1·3901, ...1·5134, obtained as a by-product in the action of quinoline ...n 1:2-dibromo*cyclo*hexane, combines with bromine to form a ...*bromide*, b. p. 138—140°/16 mm., and is oxidised by permanganate ...o adipic acid.

$\Delta^{1:3}$-*cyclo*Hexadiene combines with hydrogen bromide to form a ...ydrobromide, b. p. 80—85°/39 mm. This combines with bromine to ...rm a *tribromide*, b. p. 150°/15 mm., and is oxidised by permanganate ...to a dibasic hydroxy-acid, $C_6H_{10}O_5$, m. p. 93—94°, which distils almost ...nchanged at 240°/20 mm. The formation of this dibasic hydroxy-...id on oxidation renders improbable the constitution assigned to this ...ydrobromide by Crossley (Trans., 1904, 85, 1422). T. A. H.

Tetramethyl*cyclo*heptatriene. HANS RUPE and W. KERKOVIUS (*Ber.*, 1911, 44, 2702—2713).—The action of magnesium methyl ...dide on eucarvone yields a tetramethyl*cyclo*heptatriene,

$$CMe\begin{matrix}\diagup CMe{:}CH\cdot CMe_2 \\ \diagdown CH\cdot CH{=}CH\end{matrix} \text{ or } CMe\begin{matrix}\diagup C({:}CH_2)\cdot CH_2\cdot CMe_2 \\ \diagdown CH{-}CH{=}CH\end{matrix},$$

...hich is a tetramethyl derivative of the *cyclo*heptatriene prepared by ...adenburg (Abstr., 1883, 670) and Willstätter (Abstr., 1901, i, 223, ...9). In one instance the corresponding *tertiary alcohol*, b. p. ...—97°/11 mm., was also obtained, but this could not be obtained ...re, as it undergoes partial decomposition on distillation with forma...on of the tetramethyl*cyclo*heptatriene. Further, a slight variation ...the method of preparing the latter results in its admixture with

* and *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1102—1107.

two dimeric, isomeric methyl derivatives of dihydroeucarvone, $(C_{11}H_{18}O)_2$.

*Tetramethyl*cyclo*heptatriene*, $C_{11}H_{16}$, is a colourless, mobile oil, b. p. 67—68°/11 mm., D^{20} 0·8687, n_D^{20} 1·50660. The optical exaltation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 365, 367), +0·9, is exactly what is observed for a pair of conjugated ethylene linkings with a side-chain at one of the end carbon atoms; the fact that the three conjugated double linkings of the above formula do not give a considerably higher exaltation than 0·9 seems to be a new proof for the assumption made by Auwers and Eisenlohr (*loc. cit.*) that constitutional disturbances (side-chains) may partly or completely annul the optical anomaly of a conjugated linking. It is more stable than methylmenthatriene (compare Rupe and Liechtenhan, Abstr., 1906, i, 376) and yields a *dihydrobromide*, $C_{11}H_{18}Br_2$. When reduced by sodium in amyl alcohol solution, it yields a mixture of di- and tetra-hydro-derivatives, whilst in ethyl alcohol, it gives the pure dihydro-compound, *tetramethyl*cyclo*heptadiene*, $C_{11}H_{18}$, b. p. 64·5—65·5°/12 mm., D^{20} 0·8491, n_D^{20} 1·47643. Which pair of conjugated double linkings is thus easily reduced is not known.

The two methyl derivatives of dihydroeucarvone have the following properties: (*A*) The less readily soluble form gives shining, white, monosymmetric leaflets, m. p. 177—178°. That its *oxime*, $C_{11}H_{19}ON$, decomposing at 265°, and its *semicarbazone*, decomposing at 259°, and also those of compound *B*, are likewise dimeric is indicated by the high melting points. (*B*) This modification forms four-sided, prismatic crystals, m. p. 142—143°; its *oxime* is found to be a mixture of two compounds, m. p.'s 204—205° and 265° respectively, the latter being identical with the oxime of *A*. Unlike eucarvone, the compounds *A* and *B* decolorise permanganate in acetic acid solution only after some minutes; the conclusion is hence drawn that these compounds contain no ethylene linking, and that they are probably stereoisomerides of the structure: $CH_2 < \begin{matrix} CO—CHMe—CH\cdot CH—CHMe—CO \\ CMe_2\cdot CHMe\cdot CH\cdot CH\cdot CHMe\cdot CMe_2 \end{matrix} > CH_2$.

These results render it highly probable that methylmenthatriene contains two conjugated double linkings. T. H. P.

Δ³-Butenylbenzene. C. N. Riiber (*Ber.*, 1911, 44, 2391—2393).—Attempts to prepare Δ³-butenylbenzene, $C_6H_5\cdot CH_2\cdot CH_2\cdot CH:CH_2$, have previously given only Δ²-butenylbenzene. On condensing allyl bromide and benzyl chloride by means of sodium, it is now shown that in addition to diallyl and dibenzyl, a hydrocarbon, b. p. 64°/10 mm., is formed. This is proved to be *Δ³-butenylbenzene*, since it yields phenylpropionic acid when oxidised by permanganate in acetone.

The hydrocarbon is a mobile, strongly refractive and dispersive liquid, with an odour similar to that of cress leaves; it has D_4^{20} 0·8831, n_D^{20} 1·5059. E. F. A.

Preparation of 2:4:6-Trinitrobenzene from Halogenated Trinitrobenzenes. Jacob. Meyer (D.R.-P. 234726).—When 1-chloro-2:4:6-trinitrobenzene is vigorously boiled during two hours with finely divided copper in a neutral solvent (such as alcohol), the

...rine is eliminated and pure 2 : 4 : 6-trinitrobenzene separates from ...cooled solution. The metals capable of reacting in this manner ...copper, zinc, magnesium, brass, iron, or aluminium, whilst methyl, ...yl, or amyl alcohols, benzene, acetone, or ether can be employed as ...vent. F. M. G. M.

Barium Oxide as a Reducing Agent. Reduction of Nitro-...zene to Nitroso- and Azo-benzene, Aniline, Phenazine, and ...mmonia. TH. ZERBWITINOFF and IWAN VON OSTROMISSLENSKY (...r., 1911, 44, 2402—2409).—When nitrobenzene vapour is passed ...er a layer of barium oxide heated in a tube at 230°, nitrosobenzene ...at first formed, but the reduction goes further, and, in addition to ...e chief product, azobenzene, considerable quantities of phenazine ...d aniline and traces of ammonia are formed. Nitrobenzene is ...changed when passed over heated coal or pumice, and also when ...rium or strontium oxide is substituted for barium oxide.

p-Nitrotoluene under similar conditions gives *p*-toluidine and a ...stalline, yellowish-red azotoluene, m. p. 139°. *o*-Nitrotoluene gives ...clusively *o*-toluidine. *m*-Dinitrobenzene is not altered by barium ...ide.

With barium hydroxide and nitrobenzene only aniline and phenazine ...e formed.

The formation of nitroso- and azo-benzene is due to the tendency of ...rium to form peroxide.

The following new double compounds of phenazine are described: *...nazine-quinol*, $C_6H_4(OH)_2,2C_{12}H_8N_2$, forms orange-yellow needles, ...p. 232° (decomp.); *phenazine-resorcinol*, $C_6H_4(OH)_2,2C_{12}H_8N_2$, ...rms bright yellow needles, m. p. 213·5°; *phenazine-catechol* crystallises ...stellate aggregates of bright yellow needles m. p. 184°. E. F. A.

Quantitative Investigation of the Sulphonation of Toluene. ...ARNOLD F. HOLLEMAN and P. CALAND [with T. VAN DER LINDEN and ... P. WIBAUT] (*Ber.*, 1911, 44, 2504—2522).—The quantities of ..., *m*-, and *p*-toluenemonosulphonic acids formed by the action of ...lphuric acid on toluene under various conditions have been investi...ated. The method consisted in sulphonation of the toluene and ...ansformation of the mixture of sulphonic acids into the corre...ponding sulphonyl chlorides. The composition of the latter mixture ...as deduced from its first and second melting points.

The influence of temperature, concentration of acid, and amount of ...id was investigated. Increase of temperature favoured the produc...on of para- and meta-acid at the expense of ortho-acid. Concen...ration of acid, between the limits of 96% and 100%, appeared to be ...ithout influence. Increase in the amount of acid favoured the ...roduction of ortho-acid at low temperatures, but this influence was ...asked at higher temperatures by the effect due to rise of the latter.

The presence of *m*-toluenesulphonic acid among the products of the ...lphonation of toluene has been definitely proved by the isolation of ...-toluenesulphonamide (m. p. 107°).

The addition of potassium sulphate, mercurous sulphate, and

silver sulphate has been shown to have no influence on the course of sulphonation.

The action of chlorosulphonic acid on toluene has also been studied. *p*-Toluenesulphonic acid is again the main product.

The possible interconversion of the isomeric toluene monosulphonic acids has been investigated. *m*-Toluenesulphonic acid was found unaltered after being heated with sulphuric acid during six hours at 100°. At 35° and at 75°, the transformation of ortho- and para-acids into one another occurs very slowly. At 100° this action has a certain influence on the relative proportion of acids formed during sulphonation. H. W.

Preparation of Chloroalkylarylsulphonyl Chlorides. Badische Anilin- & Soda-Fabrik (D.R.-P. 234913).—When derivatives of *p*-toluenesulphonyl chloride are treated with phosphorus pentachloride and chlorine introduced at a temperature of 120—140°, chlorination takes place in the side-chain, yielding the corresponding chlorobenzyl derivatives.

ω-Chlorotoluene-p-*sulphonyl chloride*, $C_7H_6O_2Cl_2S$, colourless needles, m. p. 64—65°, b. p. 183—185°/15 mm., was obtained from *p*-toluenesulphonyl chloride; and *m*-toluenesulphonyl chloride furnished *ω-chlorotoluene*-m-*sulphonyl chloride*, colourless crystals, m. p. 49°, b. p. about 190°/21 mm.

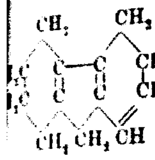
ω-2-Dichlorotoluene-p-*sulphonyl chloride*, a colourless oil, b. p. 185—190°/15·5 mm., was obtained from *o*-chlorotoluene-*p*-sulphonyl chloride, whilst 6-chlorotoluene-3-sulphonyl chloride furnished *ω-4-dichlorotoluene-3-sulphonyl chloride*, colourless crystals, b. p. 182—184°/14 mm. F. M. G. M.

Preparation of a Mixture of 1 : 4- and 1 : 5-Dichloronaphthalenes. Badische Anilin- & Soda-Fabrik (D.R.-P. 234912).—The preparation of dichloronaphthalenes has not in the past been technically satisfactory; it is now found that by working at low temperatures and in the presence of a halogen carrier that a mixture containing over 80% of 1 : 4- and 1 : 5-dichloronaphthalenes is obtained, the remainder consisting of the 1 : 2- and 1 : 7-isomerides. The naphthalene, accompanied by some freshly sublimed ferric chloride, is treated in carbon tetrachloride solution with chlorine at −10° to 0°; on fractional distillation the greater part distils at 170—190°/40 mm., and when crystallised from alcohol furnishes a colourless, crystalline powder (m. p. 50—60°) consisting of the 1 : 4- and 1 : 5-dichloronaphthalenes.

An alternative separation is to treat the crude mixture with sulphuric acid at the ordinary temperature during twenty hours, when the 1 : 4- and 1 : 5-derivatives remain unchanged, whereas the isomerides are converted into soluble sulphonic acids. F. M. G. M.

A Constituent of Coal. Amé Pictet and Louis Ramseyer (*Ber.*, 1911, **44**, 2486—2497).—A French gas coal from Montrambert was extracted with boiling benzene and also submitted to distillation under diminished pressure. The extract and distillate were fractionated and shown to contain hexahydrofluorene. On fractionating the extract it was found impossible to obtain fractions of constant

ling point, since the lower boiling fractions readily polymerise. In fractions, analysis showed the ratio C:H to be the same. For investigation, a fraction was used having a b. p. 110—120°/10 mm., 0—250° ordinary pressure, and D^{20} 0·920. This, when passed rough a red-hot tube, yielded fluorene, m. p. 112—113°. When ated with bromine in carbon disulphide solution, dibromofluorene, p. 166—167°, was formed, whilst when placed in a desiccator with mine, it became converted into monobromofluorene, m. p. 101—102°.



On oxidation with potassium permanganate, acetic, adipic, and oxalic acids were formed. Nitration yielded a mixture of products from which, on reduction and benzoylation, a dibenzoyldiaminotetrahydrofluorenol, m. p. 150°, was obtained. From the above experiments the annexed formula is proposed for hexahydrofluorene. When distilled under diminished ressure at a temperature not exceeding 450°, the same coal yielded a ries of more complex fractions in which the ratio C:H was not onstant.

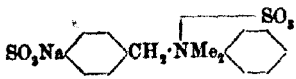
H. W.

Triphenylmethyl Peroxide. The Chemistry of Free Radicles. HEINRICH WIELAND (*Ber.*, 1911, 44, 2550—2556).—laborating his conception, already applied to $\cdot NPh_2$ and $\cdot CPh_3$ (this ol., i, 569), that a free radicle R, containing hydrogen, reacts by termolecular autoreduction and autoxidation in accordance with he scheme $4(R^{-H})H \rightarrow 2RH + (R^{-H})_2$, the author suggests that eroxides may dissociate thus: $R\cdot O\cdot O\cdot R \rightarrow 2R\cdot O\cdot$; the resulting adicle may or may not react further, as in the preceding scheme; hus the spontaneous decomposition of triphenylmethyl peroxide in oiling xylene is assumed to result in the formation of the radicle $Ph_3\cdot O\cdot$. A small portion of this is converted into triphenylcarbinol, ut the bulk of it, 60—70%, undergoes rearrangement to phenoxyiphenylmethyl, $OPh\cdot CPh_2\cdot$, by the polymerisation of which diphenylenzpinacone, the chief product of the decomposition of the peroxide, s formed. *Benzpinaconediphenyl ether*, $OPh\cdot CPh_2\cdot CPh_2\cdot OPh$, forms olourless plates, and has m. p. about 196°, darkening at 135°, by the sual process, but when heated in carbon dioxide, it becomes yellow at 50° and melts at 215° to a garnet-red liquid. When reduced by zinc nd boiling acetic acid, it is converted into phenol and benzhydryl cetate, together with a little *substance*, m. p. 198°, which probably as the constitution $OPh\cdot CPh_2\cdot C_6H_4\cdot CHPh\cdot OPh$.

When heated at 230—240° in the absence of air, benzpinaconediphenyl ether undergoes the reverse change to phenoxydiphenylmethyl, which, in accordance with the preceding scheme (except that the phenoxy-group wanders instead of a hydrogen atom), is converted into tetraphenylethylene and *diphenoxydiphenylmethane*, $CPh_2(OPh)_2$, m. p. 132°; the latter is readily hydrolysed to phenol and benzophenone by boiling acetic and concentrated hydrobromic acids. Since a little phenol and benzophenone are obtained by the depolymerisation of benzpinaconediphenyl ether by heat, especially in boiling xylene, it is probable that a portion of the phenoxydiphenylmethyl suffers the

normal autoreduction and autoxidation, yielding substances from which the phenol and benzophenone are produced. C. S.

Preparation of Phenylbenzyldimethylammoniumdisulphonic Acid. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 234915 and 234916).—*Sodium phenylbenzyldimethylammoniumdisulphonate* (annexed formula), a yellow, hygroscopic powder, is prepared by heating sodium benzylmethylanilinedisulphonate with



methyl sulphate at 50°, and subsequently evaporating under reduced pressure; when heated with aqueous ethylaniline, it furnishes benzylethylanilinesulphonic acid and dimethylaniline-3-sulphonic acid (dimethylmetanilic acid). The second patent states that the methyl sulphate can be replaced by methyl *p*-toluenesulphonate (or other methyl esters), in which case calcium benzylmethylanilinedisulphonate in the presence of calcium carbonate (or hydroxide) is employed, and the mixture heated at 60°; after separation of the toluenesulphonic acid by known methods, *calcium phenylbenzyldimethylammoniumdisulphonate* is obtained as a yellow powder, which is readily soluble in water. F. M. G. M.

Kinetics of Ammonium Salts. HANS VON HALBAN (*Zeitsch. physikal. Chem.*, 1911, 77, 719—734).—Polemical against Wedekind and Paschke (compare Abstr., 1909, ii, 722; Wedekind and Paschke, Abstr., 1908, i, 723; this vol., i, 628). The contention of these investigators that the rate of decomposition of dissolved quaternary ammonium salts is related to the dissociating power of the solvent is not valid. As already pointed out (*loc. cit.*), the reactions are relatively slow in solvents containing hydroxyl groups. The influence of the corresponding nitrate on the rate of decomposition of *d*-phenylbenzylmethylpropylammonium iodide is much smaller than Wedekind and Paschke state, and an alternative explanation of this effect is given. The very small temperature-coefficient (1·02 for a rise of temperature of 10°) given by these authors for the rate of formation of a quaternary ammonium salt is due to experimental error; the true value is 1·7.

Phenylbenzyldiethylammonium iodide forms a crystalline compound with chloroform, and *p*-bromophenylbenzyldimethylammonium iodide a similar compound with bromoform, which contains a molecule of the solvent. In contrast to solutions in chloroform, quaternary ammonium salts are only slightly polymerised in tetrachloroethane. G. S.

The Metallic Salts of Trinitrophenols and Trinitrocresols. HERMANN KAST (*Zeitsch. ges Schiess-sprengstoffwesen*, 1911, 6, 7—9, 31—34, 67—70. Compare *Annalen*, 1843, 48, 336; *Zeitsch. Chem.* 1865, 189).—A description of the preparation of the following compounds in crystalline form, with special details as to their explosive qualities.

Salts of picric acid.—Potassium, ammonium, and sodium: reddish-yellow needles, the latter containing one molecule of water of crystallisation.

Calcium, $(C_6H_2O_7N_3)_2Ca,3H_2O$ (also 5 or $10H_2O$); *barium*, $(C_6H_2O_7N_3)_2Ba,3$ or $5H_2O$; *magnesium*, $(C_6H_2O_7N_3)_2Mg,3H_2O$ (also or $6H_2O$), two mols. of which persist until 130°, and *zinc*, $(C_6H_2O_7N_3)_2Zn,8H_2O$ (also 2, 6 or $9H_2O$), two mols. of which persist until 130°, all form reddish-yellow needles. *Ferrous*,

$(C_6H_2O_7N_3)_2Fe,7$ or $8H_2O$,

transparent, green leaflets. *Ferric*, $(C_6H_2O_7N_3)_3Fe,11H_2O$, reddish-yellow crystals. *Cuprous*, $(C_6H_2O_7N_3)_2Cu,5H_2O$ (also 4 or $11H_2O$), two mols. of which persist until 130°, forms small, greenish-yellow needles. *Silver*, reddish-yellow, glistening needles unstable in light. *Aluminium*, $(C_6H_2O_7N_3)_2Al(OH),7H_2O$, small, reddish-yellow needles. *Lead*, $(C_6H_2O_7N_3)_2Pb,1$ or $4H_2O$, a yellow, crystalline powder.

Salts of trinitrocresol.—*Potassium*, $C_7H_4O_7N_3K$. *Sodium*,

$C_7H_4O_7N_3Na,2H_2O$,

small, yellow needles. *Ammonium* and *calcium*, $(C_7H_4O_7N_3)_2Ca,4H_2O$, reddish-yellow needles. *Barium*, $(C_7H_4O_7N_3)_2Ba,H_2O$, small, sulphur-yellow leaflets. *Magnesium* and *zinc*, reddish-yellow powders, with H_2O, three of which in the zinc salt persist until 130°. *Cuprous*, $(C_7H_4O_7N_3)_2Cu,2H_2O$, small, greenish-yellow needles, is stable until 1[illegible]°. Silver, reddish-yellow needles (compare Abstr., 1885, 531). *Aluminium*, $(C_7H_4O_7N_3)_2Al(OH),5H_2O$, reddish-yellow needles, darkening in sunlight. *Lead*, $(C_7H_4O_7N_3)_2Pb,H_2O$, sulphur-yellow leaflets. *Ferrous*, $(C_7H_4O_7N_3)_2Fe,2H_2O$, glistening, greenish-yellow needles, and *ferric*, brown crystals, decomposed by boiling water. F. M. G. M.

Preparation of 4-Chloro-6-nitro-2-aminophenol. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234742).—When 4-chloro-2-acetylaminophenol is treated with dilute nitric acid, 4-*chloro-6-nitro-2-acetylaminophenol*, m. p. 150—160°, is produced, which when hydrolysed by alkali hydroxides yields 4-chloro-6-nitro-2-aminophenol as a yellowish-brown powder. F. M. G. M.

Derivatives of 1:2-Dimethylbenzene [o-Xylene]. II. EMIL DIEPOLDER (*Ber.*, 1911, **44**, 2498—2503. Compare Abstr., 1909, i, 6[illegible]).—The phenylhydrazone of the o-4:5-xyloquinone described previously, when treated with sodium hyposulphite in alcoholic solution, yields 5-amino-o-4-xylenol; the *acetyl* derivative crystallises in thin plates, which sinter at 184°, m. p. 190·5—191°, and when heated gives 5-*vinylideneamino-o-4-xylenol*, white needles, m. p. 93—94°.

5-*Acetylamino-o-4-xylenyl acetate* forms fine, white, silky needles, m. p. 156—157°, and 5-*diacetylamino-o-4-xylenyl acetate* crystallises in hexagonal plates, m. p. 100·5—101·5°.

o-Aminophenol when treated with acetic anhydride and sodium acetate yields o-*diacetylaminophenyl acetate* in long, colourless needles, m. p. 78—79°.

4:5-*Dihydroxy-m-xylene*, obtained by the reduction of o-4:5-xyloquinone with aqueous sulphurous acid or sodium hyposulphite, forms colourless, slender prisms sintering at 85°, m. p. 87—88°.

Attempts to prepare a colourless modification of o-4:5-xyloquinone were fruitless. H. W.

Chloroguaiacols. TEMISTOCLE JONA and G. B. POZZI (*Gazzetta*, 1911, 41, i, 722—737).—5-*Aminoguaiacol hydrochloride*, $C_7H_{10}O_2NCl$, from 5-nitro-1-acetylguaiacol (compare Cousin, Abstr., 1899, i, [illegible]), forms pale greenish-white crystals. 5-*Aminoguaiacol*, $C_7H_9O_2N$, was obtained in grey crystals, m. p. 125—127°, which were not quite pure; it gives a reddish-brown coloration with ferric chloride. 5-*Benzoylaminoguaiacol benzoate*, $C_{21}H_{17}O_4N$, forms colourless crystals, m. p. 162—164°, and does not give a coloration with ferric chloride. 5-*Acetylaminoguaiacol*, $C_9H_{11}O_3N$, forms colourless crystals, m. p. 116—119°, and gives the phenol reaction with ferric chloride. 5-*Chloroguaiacol*, $C_7H_7O_2Cl$, obtained by the Sandmeyer reaction from aminoguaiacol, has b. p. 237—239°/760 mm. (corr.), m. p. 161—163°. It gives a yellow coloration with ferric chloride. 5-*Chloroguaiacol benzoate*, $C_{14}H_{11}O_3Cl$, crystallises in long, colourless needles, m. p. 56—58°. 5-*Chloroguaiacol acetate*, $C_9H_9O_3Cl$, crystallises in colourless leaflets, m. p. 42—44°. 5-*Chloroguaiacolethyl ether*, $C_9H_{11}O_2Cl$ (prepared with ethyl iodide), forms colourless crystals, m. p. 49—51°.

4-Aminoguaiacol acetate is obtained by reducing with phenylhydrazine the acetyl derivative of benzeneazoguaiacol.

4-*Acetylaminoguaiacol*, $C_9H_{11}O_3N$ (from 4-aminoguaiacol), forms colourless crystals, m. p. 111—113°, and gives the phenol reaction with ferric chloride. 4-*Chloroguaiacol*, $C_7H_7O_2Cl$ (prepared by the Sandmeyer reaction from 4-aminoguaiacol acetate), is a colourless crystalline substance, m. p. 158—161°, b. p. 241—243°/760 mm. (corr.). Its *benzoyl* derivative, $C_{14}H_{11}O_3Cl$, crystallises in colourless scales having a mother-of-pearl lustre, m. p. 79—80°.

The benzoyl derivative of chloroguaiacol obtained by Peratoner and Ortoleva (Abstr., 1898, i, 641) had m. p. 76—77°, and was probably identical with the derivative just described. R. V. S.

Preparation of 1 : 4-Dihydroxynaphthalene Monoalkyl Ethers. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 234411).—A satisfactory yield of 1 : 4-dihydroxynaphthalene monoalkyl ethers can be obtained by heating 4-amino-α-naphthol hydrochloride with alcohol during twelve hours at 170—180°. When methyl alcohol is employed under these conditions, 200 parts of the aminonaphthol yield 120—130 parts of the *monomethyl ether*, reddish-white crystals, m. p. 131°. F. M. G. M.

Some Derivatives of Hydroxyquinol. IV. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 18—25. Compare this vol., i, 68, 305).—In the course of attempts to demonstrate the structure of 2 : 4 : 5-trimethoxypropiophenone and of its dimethyl ether, previously described, the authors have prepared some new derivatives of these substances. Trimethoxypropiophenone is not acted on by bromine and sodium hydroxide (compare Störmer and Wehln, Abstr., 1903, i, 40).

Hydroxyquinol trimethyl ether may be prepared with good yield by the action of methyl sulphate on triacetylhydroxyquinol, a concentrated solution of sodium hydroxide being added in small portions. Hexamethoxydiphenyl is not formed when the reaction is carried out in this way.

The 2-hydroxy-4 : 5-dimethoxypropiophenone previously mentioned crystallises in small, colourless needles, m. p. 124—126° (softening at 90°). The *acetyl* derivative, $C_{13}H_{16}O_5$, also crystallises in needles, m. p. 117—118°. The *benzoyl* derivative, $C_{18}H_{18}O_5$, forms long needles, m. p. 110—111°.

2 : 4 : 5-*Trimethoxypropiophenonephenylhydrazone* has m. p. 113°. 2 : 4 : 5-*Trimethoxypropiophenonemonoxime* (prepared with amyl nitrite), $C_{12}H_{15}O_5N$, crystallises in scales having a slight yellowish-green colour, and has m. p. 146—148°. It gives a deep reddish-brown coloration with an alcoholic solution of nickel acetate. When it is treated with hydroxylamine hydrochloride the *dioxime*, $C_{12}H_{16}O_5N_2$, is formed, which crystallises in prismatic needles, m. p. 206—207°. An alcoholic solution of the substance yields with an alcoholic solution of nickel acetate a bright red precipitate; with ammonium palladichloride it gives a pale yellow substance; with ferrous sulphate in the presence of pyridine an intense red coloration and a red precipitate are produced. The substance seems, therefore, to be a *syn*dioxime (compare Tschugaeff, Abstr., 1908, i, 554). When the above monoxime is treated with phenylhydrazine, the *oxime-phenylhydrazone*, $C_{18}H_{21}O_4N_3$, is obtained as a white, crystalline powder, m. p. 246—248°. By boiling the monoxime, dioxime, or oxime-phenylhydrazone with dilute acids, small quantities of a crystalline *substance*, m. p. 133°, are obtained.

R. V. S.

Some Derivatives of Hydroxyquinol. V. GUIDO BARGELLINI and S. AURELI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 118—124. Compare this vol., i, 305).—Hydroxy-ketones related to hydroxyquinol have been prepared by the action of persulphates on less highly oxygenated phenols in alkaline solution (compare Kumagai and Wolffenstein, Abstr., 1908, i, 159). It is further found that the saponification of 2 : 4 : 5-trimethoxyacetophenone by means of hydrobromic acid (compare Stoermer, Abstr., 1908, i, 190) yields 2 : 4-dihydroxy-5-methoxyacetophenone.

The action of potassium persulphate or of ammonium persulphate on 2-hydroxy-4-methoxyacetophenone (paeonol) in alkaline solution under diverse conditions yields 2 : 5-*dihydroxy-4-methoxyacetophenone*, $C_9H_{10}O_4$, which crystallises in white scales having a yellow tinge, m. p. 164°. When dissolved in concentrated sulphuric acid, it gives a yellowish-green coloration. Its aqueous solution gives with ferric chloride a red coloration. The *acetyl* derivative, $C_{13}H_{14}O_6$, forms small, colourless needles, m. p. 118—119°. The *benzoyl* derivative is a yellowish-white, crystalline powder, m. p. 215°. When sodium peroxide is used instead of a persulphate in the above oxidation, the paeonol remains unchanged, whilst when hydrogen peroxide is employed a mixture of products is obtained. Esterification of 2 : 5-dihydroxy-4-methoxyacetophenone with methyl sulphate yields both the trimethoxy- and dimethoxy- derivatives. The former can be extracted with ether from the alkaline solution, and is identical with the 2 : 4 : 5-trimethoxyacetophenone, m. p. 101—102°, previously described (Bargellini and Avrutin, this vol., i, 68). From the alkaline liquid after acidification, 2-*hydroxy-4 : 5-dimethoxyacetophenone*, $C_{10}H_{12}O_4$,

can be extracted with ether; it crystallises in yellowish-white needles, m. p. 114—115°. Its aqueous solution gives a green coloration with ferric chloride. The *acetyl* derivative, $C_{12}H_{14}O_5$, forms small, colourless needles, m. p. 146—147°. With anisaldehyde, 2-hydroxy-4:5-dimethoxyacetophenone yields 2′-*hydroxy* 4:4′:5′-*trimethoxychalkone*, which crystallises in small, red needles, m. p. 130°. It dissolves in concentrated sulphuric acid, giving an intense orange-yellow coloration.

When trimethoxyacetophenone in acetic acid solution is boiled for two hours with hydrobromic acid (D 1·47), 2:4-*dihydroxy-5-methoxyacetophenone*, $C_9H_{10}O_4$, is produced; it forms yellowish-white needles, m. p. 166°. Its aqueous solution gives a red coloration with ferric chloride. The *acetyl* derivative, $C_{13}H_{14}O_6$, crystallises in long, colourless needles, m. p. 127—128°.

R. V. S.

A Nitroso-compound of Dimethoxyphenol, and its Derivatives. RUDOLF FABINYI and TIBOR SZÉKI (*Ber.*, 1911, 44, 2293—2298).—The substance obtained by boiling asaronic acid in aqueous solution with sodium nitrite, and formerly supposed to be 4:5-dimethoxy-*o*-benzoquinoneoxime or its tautomeride (Abstr., 1907, i, 45), is now shown to be 2:5-dimethoxy-1:4-benzoquinoneoxime or the tautomeric 4-nitroso-2:5-dimethoxyphenol, and a number of its derivatives are described. The substance on repeated crystallisation from hot acetic acid forms transparent, lustrous citron-yellow needles identical in composition with the red form described previously.

On methylation with methyl sulphate, it gives 4-*nitroso-1:2:5-trimethoxybenzene*, m. p. 191°, which crystallises in long, reddish-yellow needles from alcohol. The reduction to 4-amino-2:5-dimethoxyphenol, m. p. 157° (*loc. cit.*), is best effected by ammonia and hydrogen sulphide; the *acetylamino*-compound, m. p. 180°, crystallises from boiling water, and the *diacetyl* derivative, m. p. 190°, from either water or boiling alcohol; the *dipropionyl* derivative, m. p. 131°, also crystallises from alcohol. On oxidation with 50% nitric acid the aminodimethoxyphenol yields 2:5-dimethoxy-1:4-benzoquinone (compare Schüler, Abstr., 1907, i, 700), and on treatment with ethyl chlorocarbonate in alcohol gives *ethyl 4-hydroxy-2:5-dimethoxyphenylaminoformate*, m. p. 143°, which crystallises from benzene in glancing leaflets, and is readily soluble in alcohol, chloroform, or acetic acid, the *acetyl* derivative of this, m. p. 135°, crystallises from hot alcohol, and the *carboxymethyl ether*, $CO_2H{\cdot}CH_2{\cdot}O{\cdot}C_6H_2(OMe)_2{\cdot}NH{\cdot}CO_2Et$, m. p. 108°, obtained by condensation with ethyl bromoacetate in presence of sodium and alcohol, crystallises from alcohol.

4-*Acetylamino-2:5-dimethoxyphenoxyacetic acid*,

$$NHAc{\cdot}C_6H_2(OMe)_2{\cdot}O{\cdot}CH_2{\cdot}CO_2H,$$

m. p. 172°, obtained by condensing ethyl bromoacetate with 4-hydroxy-2:5-dimethoxyacetanilide, forms colourless crystals from alcohol.

Several of the substances described exert an antipyretic action, which is, however, less marked than that due to phenacetin.

T. A. H.

Aromatic Tellurinium Compounds with the same Hydrocarbon Residue. CHARLES LEDERER (*Ber.*, 1911, 44, 2287—2293).
Tellurium tetrachloride reacts with the Grignard reagent to form tellurinium compounds containing three aromatic hydrocarbon residues. These react in part with the Grignard reagent present to form the corresponding diaryl tellurides and diaryl hydrocarbons, thus: $R_3TeCl + R \cdot MgBr = R_2Te + R_2 + MgClBr$. In addition, the diaryltelluride so formed reacts with hydrochloric acid subsequently added, in presence of air, to form some diaryltellurinium dichloride, which in turn is decomposed on addition of water, forming a basic chloride, thus:

$$TeR_2 + 2HCl + O = TeR_2Cl_2 + H_2O = TeR_2Cl \cdot OH + HCl.$$

In these equations R represents an aromatic hydrocarbon residue. In certain cases irregularities were observed. With magnesium o-tolyl iodide, no di-*o*-tolyl was formed, but, instead, an unidentified high-boiling hydrocarbon. With magnesium *p*-tolyl bromide, the di-*p*-tolyl obtained was not identical with that of Weiler (Abstr., 1899, i, 490). A description is given of the method used for the separation of all the substances formed.

Triphenyltellurinium iodide, $TePh_3I$, sinters at 245°, has m. p. 247—249°, and crystallises from hot water in small needles. The corresponding *bromide*, m. p. 259—260°, separates from hot water in small prisms. The *chloride*, m. p. 244—245°, crystallises from dry alcohol on addition of ether in long, slender needles.

Tri-p-tolyltellurinium iodide, m. p. 232—233° (decomp.), crystallises from alcohol in six-sided tablets. The *bromide*, m. p. 265—266° (decomp.), crystallises from water or from alcohol on addition of ether. The *chloride*, m. p. 260—261°, crystallises in small prisms from dry alcohol on addition of ether.

Tri-o-tolyltellurinium iodide, m. p. 195—196°, forms small, four-sided columns from water or alcohol on addition of ether. Its aqueous solution is precipitated by picric acid. T. A. H.

Preparation of ω-*p*-Alkylhydroxyphenylethylamines and their *N*-Alkyl Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234795).—It is found that ω-*p*-alkylhydroxyphenylethylamines can be readily prepared by treating primary *p*-alkylhydroxyphenylethyl alcohols with phosphorus pentahalides and subsequently heating the ω-*p*-alkylhydroxyphenylethyl halide so obtained with ammonium hydroxide (or the required alkylamine) in a closed vessel at 100°.

p-Methoxyphenylethyl alcohol, m. p. 22°, b. p. 143°/13 mm. (prepared from ethylene chloride and magnesium *p*-anisyl bromide), furnished under these conditions a 50—60% yield of ω-*p*-methoxyphenylethylamine, and when dimethylamine was employed, an 80% yield of ω-*p*-methoxyphenylethyldimethylamine; the intermediate *chloride* has b. p. 100—105°/7 mm.

p-Ethoxyphenylethyl alcohol, prepared from ethylene chlorohydrin and magnesium *p*-phenetyl bromide, can also be employed in the foregoing reaction; it has m. p. 40° and b. p. 135—140°/7 mm.; the intermediate *chloride* has b. p. 125—130°/7 mm. F. M. G. M.

Phytosterols of Soy Bean. HERMANN MATTHES and A. DAHLE (*Arch. Pharm.*, 1911, **249**, 436—444. Compare this vol., i, 831; Klobb and Block, Abstr., 1907, i, 521; Keimatsu, this vol., i, 766).—Soy bean oil contains 0·7% of unsaponifiable matter, of which 55% is solid and crystalline, and is composed of stigmasterol 2·4%, and a new phytosterol 97%, and 45% is liquid.

The crude unsaponifiable matter was mixed with light petroleum and the mixture strongly cooled, when it separated into (1) a solid, crystalline product; (2) a solution in light petroleum of a viscous, brown material. The solid product was acetylated and the acetylated product brominated in ether solution, when stigmasterol acetate tetrabromide, m. p. 205—206° (compare Windaus and Hauth, Abstr., 1907, i, 129), separated. The portion of the brominated product soluble in ether was recovered in crystalline form by gradual addition of water to its solutions in alcohol. It proved to be *phytosterol acetate dibromide*, $C_{29}H_{46(or\ 48)}O_2Br_2$, m. p. 125°, and on reduction and subsequent hydrolysis gave the corresponding *phytosterol*, $C_{27}H_{46(or\ 48)}O,H_2O$, m. p. 139°, $[\alpha]_D^{15}$ − 22·83°.

The liquid product had iodine number 124·4, n_D^{20} 1·48[illegible], $[\alpha]_D$ 0°, and gave the colour reactions of the phytosterols. On treatment with digitonin (compare Windaus, Abstr., 1909, i, 172) a small amount of the material separated as a *crystalline additive product*, $[\alpha]_D^{15}$ − 44·66° in methyl alcohol, but no separation of the liquid into its components was thereby effected. The liquid has the same empirical composition as the phytosterol referred to above. T. A. H.

Action of Chlorine on "Saccharin." PASQUALE BERTOLO (*Gazzetta*, 1911, **41**, i, 698—705).—When "saccharin" is subjected to the prolonged action of nascent chlorine (from hydrochloric acid and potassium chlorate), *o*-chlorobenzoic acid is obtained. When the duration of the action is more limited, however, a substance is obtained to which the constitution of *potassium* o-*iminosulphobenzoic acid*, $NH:SO(OK)\cdot C_6H_4\cdot CO_2H$, is ascribed. In this case "saccharin" is boiled with dilute hydrochloric acid, and potassium chlorate is added from time to time until the "saccharin" is completely dissolved, and the boiling is then continued for a few minutes to expel excess of chlorine. The above-mentioned substance, $C_7H_6O_4NSK$, crystallises from the solution, after concentration, in the form of transparent, colourless, tabular, rhombic crystals [S. Di Franco: $a:b:c$ = 1·46335 : 1 : 1·79093], m. p. 285—286°. The *barium* salt,

$$C_6H_4<\begin{matrix}CO_2\text{——————}\\ SO(:NH)\cdot O\end{matrix}>Ba,$$

crystallises with $1\frac{1}{2}H_2O$, which it loses at 110°. From it the free acid may be obtained. When the potassium salt is boiled with 5% potassium hydroxide, ammonia is evolved, and *potassium* o-*sulphobenzoate* is obtained. *Barium sulphobenzoate*, $C_7H_4O_5SBa,2H_2O$, was also prepared. R. V. S.

Preparation of Esters of Cinnamic Acid. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235357).—*Ethylene cinnamate*, a colourless, odourless oil, b. p. 190—195°/11 mm., is prepared by

heating together equal quantities of ethylene glycol and cinnamic acid during thirty hours at 140° in the presence of concentrated sulphuric acid. *Glycerol monocinnamate*, a yellow, oily liquid, and *glycerol chlorohydrin ethoxycinnamate*, a yellow liquid, and other substances allied to the constituents of Peru balsam are discussed in the original. F. M. G. M.

Refraction of Light by *allo*- and *iso*-Cinnamic Acids. Hans Stobbe and Fritz Reuss (*Ber.*, 1911, **44**, 2735—2739).—Two specimens of *allo*cinnamic acid were examined: (1) m. p. 68°, prepared by the action of hydrogen on phenylpropiolic acid in presence of colloidal palladium, and (2) m. p. 67—68°, prepared from an aniline salt.

With acid (1) the following refractometric measurements were made on the melted acids: (*a*) of *allo*cinnamic acid from 71·7° to 24°; (*b*) of *iso*cinnamic acid, m. p. 58°, from 70·7° to 55·8°, and (*c*) of *iso*cinnamic acid, m. p. 42°, from 45·8° to 51·1°. The results, plotted against the temperature, all fell on a straight line, so that the refraction of all three acids is continuous and diminishes proportionally with the temperature, as happens with compounds known to be chemical individuals. The results obtained with *allo*cinnamic acid (2) from 77·3° to 22·6° also fell on a straight line with the same slope as, and only very slightly distant from, that of the (1) acids. Fused *allo*- and *iso*-cinnamic acids are hence to be regarded as optically identical. T. H. P.

Transformations of *allo*- and *iso*-Cinnamic Acids in the Fused and Crystalline States. Hans Stobbe (*Ber.*, 1911, **44**, 2739—2754. Compare preceding abstract).—The author has confirmed and extended the observations of Liebermann (Abstr., 1903, i, 255; 1909, i, 303; 1910, i, 36, 175), Biilmann (Abstr., 1909, i, 155, 382; 1910, i, 346), Erlenmeyer (Abstr., 1891, 200; 1896, i, 46), Erlenmeyer, jun. (Abstr., 1906, i, 429; 1907, i, 318; 1909, i, 156, 647, 648), Paal and Hartmann (Abstr., 1909, i, 926), and Stoermer (Abstr., 1910, i, 114) on *allo*- and the two *iso*-cinnamic acids. In the experiments described, extreme care was taken to avoid accidental seeding of the fused or crystalline masses under examination.

By crystal-seeding, the crystalline acid m. p. 42° can be converted into that with m. p. 68° (with development of considerable heat) or 58°, and the latter into that with m. p. 68°.

When the crystalline 42°-acid is heated in a sealed tube for eighty hours at 37°, or the 58°-acid for thirty hours at 52°, no change occurs; but the 42°-acid is transformed completely into the 68°-acid in five minutes at −80° and almost instantaneously at −180°; with the 58°-acid similar conversion takes place in three hours at −80° and in ten minutes at −180°. The 68°-acid undergoes no change at either −80° or −180°, so that, in all cases, the most labile acid (42°) is converted, by grinding (Liebermann, *loc. cit.*) or cooling, into the stable *allo*-acid more rapidly than is the less labile form (58°). The two labile acids appear to be only metastable forms of a single chemical compound, trimorphous *cis*-cinnamic acid.

If a few milligrams of the fused 68°-acid, heated for 0·5—5 minutes to 72—80°, are cooled to the ordinary temperature or to −14°, the result was almost always the 42°-acid, but occasionally the 58°-acid, but 0·05—1·0 gram of the 68°-acid, on heating to 80—105° for ten minutes or for several hours, and then cooling to the ordinary temperature or to −14°, solidifies to the 68°-acid more frequently than to the 42°-acid.

The observation of Liebermann and of Biilmann, that the fused 42°- and 58°-acids always solidify to the 42°-acid on cooling to the ordinary temperature or to 0°, is confirmed, but if the cooling is effected in a mixture of ice and salt, sometimes the 42°-acid and sometimes the 58°-acid separates; separation of the former can always be recognised by the slowness with which crystallisation occurs. Further, if the fusion from the 42°- or 58°-acid is immersed in a mixture of ether and carbon dioxide or in liquid air, it forms an amorphous, glassy mass with a concave, funnel-shaped surface, and shows no tendency to crystallise, even after some hours; but if the mass is removed from the cooling mixture so that its temperature rises, the concavity of the surface gradually disappears, and it undergoes a usually sudden and always rapid crystallisation, the 58°-acid invariably separating, so that these two labile acids, which in the fused condition are optically identical, can be mutually interconverted without any seeding being necessary.

Results similar to the above were obtained on cooling the fused 68°-acid in ice and salt, ether and carbon dioxide, or liquid air, the only divergence being that occasionally, in additton to the 42°- or 58°-acid, the 68°-acid also separated.

Optical identity (compare preceding abstract) of these three acids does not, therefore, always present itself, and the conclusion is drawn that there are in reality two chemically different isomeric acids, (1) monomorphous *allo*cinnamic acid, m. p. 68°, and (2) dimorphous *iso*cinnamic acid, m. p. 42° and 58°. T. H. P.

Oxidation of *allo*-Cinnamylideneacetic Acid. C. N. Riiber (*Ber.*, 1911, **44**, 2389—2391).—Doebner (Abstr., 1890, 1274) has shown that cinnamylideneacetic acid, when cautiously oxidised with potassium permanganate, is converted into benzoic acid and racemic acid. It is now shown that *allo*-cinnamylideneacetic acid,

$$CHPh:CH\cdot CH:CH\cdot CO_2H,$$

under similar conditions is converted into benzoic acid and meso-tartaric acid. The two cinnamylideneacetic acids are accordingly related in the same manner as fumaric and maleic acids, the isomerism being due to the double linking 1:2. The double linking 3:4 is hardly concerned, since both isomerides when distilled with quinoline give the same stable phenylbutadiene. E. F. A.

Reaction between Organomagnesium Compounds and Cinnamylidene Esters. III. Reactions with the Isomeric Methyl Esters of Cinnamylideneacetic Acid. Grace P. Reynolds (*Amer. Chem. J.*, 1911, **46**, 198—211. Compare Abstr., 1907, i, 852; 1908, i, 988).—The action of magnesium alkyl or aryl

...sides as the isomeric methyl cinnamylideneacetates may give rise ... three different classes of compounds: (i) tertiary alcohols,

$$CHPh:CH\cdot CH:CH\cdot CR_2\cdot OH,$$

...ed by replacement of the methoxy-group and addition of the ...nesium compound to the carbonyl group; (ii) unsaturated ketones, ...Ph:CH·CHR·CH_2·COR, produced by 1:4-addition and simultaneous ...placement of the methoxy-group; (iii) unsaturated esters of the ...e CHPh:CH·CHR·CH_2·CO_2Me, formed by 1:4-addition only. It is ...nd that the nature of the product depends on the magnesium ...mpound employed. Whilst magnesium phenyl bromide forms only ... unsaturated ketone and magnesium ethyl bromide a tertiary alcohol, ...e action of magnesium benzyl bromide yields a mixture of compounds ...longing to all three classes.

Methyl allocinnamylideneacetate, CHPh:CH·CH:CH·CO_2Me, obtained ...y the action of methyl alcohol and hydrogen chloride on the corre...sponding acid, is a liquid, which solidifies at −15° to a white, crystal...line mass, and is partly converted into the isomeric ester by distillation ...under diminished pressure. Both esters react with magnesium phenyl ...romide, yielding β-phenyl-β-styrylpropiophenone (Kohler, Abstr., ...905, i, 258), which is converted by the further action of magnesium ...henyl bromide into *αγεε-tetraphenyl-Δ^α-penten-ε-ol*,

$$CHPh:CH\cdot CHPh\cdot CH_2\cdot CPh_2\cdot OH.$$

...he latter compound forms slender, white needles, m. p. 134°, and is ...xidised by potassium permanganate to benzoic acid and *αγγ-triphenyl-butyrolactone*, $\begin{matrix}CHPh\cdot CO\\ CH_2\cdot CPh_2\end{matrix}\!\!>\!O$, which crystallises in long, iridescent ...edles, m. p. 157°. Experiments carried out with the isomeric ...ethyl cinnamylideneacetates under similar conditions showed that ...e *allo*-ester reacts with magnesium phenyl bromide more readily than ...e isomeride.

The interaction of magnesium benzyl bromide and methyl cinn...amylideneacetate yields (1) *αζ-diphenyl-γ-benzyl-Δ^α-hexen-ε-one*,

$$CHPh:CH\cdot CH(C_7H_7)\cdot CH_2\cdot CO\cdot CH_2Ph,$$

...hich is a viscid, lemon-yellow liquid, b. p. 265°/15 mm., and yields ... *dibromide*, $C_{26}H_{24}OBr_2$, m. p. 165·5°; (2) *αζ-diphenyl-ε-benzyl-Δ^{αγ}-...exadien-ε-ol*, CHPh:CH·CH:CH·C(CH_2Ph)$_2$·OH, a mobile, lemon-...yellow liquid, b. p. 200°/10 mm.; the *tetrabromide* forms slender needles, ...m. p. 227° (decomp.); (3) *β-benzyl-γ-benzylidenebutyric acid*,

$$CHPh:CH\cdot CH(C_7H_7)\cdot CH_2\cdot CO_2H,$$

...hich crystallises in heavy, iridescent plates, m. p. 144°, yields a ...rystalline *methyl* ester, m. p. 66°, and is oxidised by potassium ...ermanganate in aqueous sodium carbonate solution to benzoic and ...enzylsuccinic acids.

α-Phenyl-ε-ethyl-Δ^{αγ}-heptadien-ε-ol, CHPh:CH·CH:CH·CEt_2·OH, ...btained by the action of magnesium ethyl bromide on methyl ...innamylideneacetate, is a pale yellow, mobile liquid, b. p. 169°/...0 mm. It is accompanied by a viscid liquid, b. p. 278—285°/10 mm., ...hich deposits an *ester*, crystallising in needles, m. p. 136°, when kept. ...ydrolysis of the latter substance with alcoholic potassium hydroxide ...ields an acid, m. p. 230°. The constitution of the last-mentioned ...ubstances has not been determined. F. B.

Reaction between Unsaturated Compounds and Organic Zinc Compounds. II. ELMER P. KOHLER, GERTRUDE L. HERITAGE, and A. L. MACLEOD (*Amer. Chem. J.*, 1911, **46**, 217—236).—It has been shown previously (Abstr., 1910, i, 484) that the zinc compounds of esters of bromoacetic acid react with αβ-unsaturated ketones, yielding unsaturated hydroxy-acids, and from this the conclusion was drawn that the addition of organo-zinc compounds occurs only in the 1 : 2-position. The present paper deals with the interaction of phenyl styryl ketone and the zinc derivatives of the methyl or ethyl esters of α-bromopropionic, α-bromobutyric, α-bromo*iso*butyric, and bromomalonic acids. It is found that both 1 : 2- and 1 : 4-addition may take place with the formation of the compounds :

$$\text{(I) } CHPh\!:\!CH{\cdot}CPh(O{\cdot}ZnBr){\cdot}CHR{\cdot}CO_2R' \text{ and}$$
$$\text{(II) } ZnBr{\cdot}O{\cdot}CPh\!:\!CH{\cdot}CHPh{\cdot}CHR{\cdot}CO_2R',$$

the relative proportions of the two products depending on the nature of the bromo-ester, $CHRBr{\cdot}CO_2R'$, employed.

When decomposed with acids, the zinc compounds of the first type yield esters of unsaturated hydroxy-acids,

$$CHPh\!:\!CH{\cdot}CPh(OH){\cdot}CHR{\cdot}CO_2R',$$

whilst those belonging to the second type give rise to esters of ketonic acids of the formula : $COPh{\cdot}CH_2{\cdot}CHPh{\cdot}CHR{\cdot}CO_2R'$. The zinc compounds produced by 1 : 4-addition may also yield unsaturated lactones according to the scheme :

$$\begin{array}{ll} CHPh{\cdot}CH{=\!=}CPh \\ CHR{\cdot}CO_2R' \quad O{\cdot}ZnBr \end{array} \rightarrow \begin{array}{ll} CHPh{\cdot}CH\!:\!CPh \\ CHR{\cdot}CO{-}O \end{array} + OR'{\cdot}ZnBr$$

The relative amounts of the products formed by 1 : 2- and 1 : 4-addition were determined by heating the mixtures with aqueous sodium carbonate, whereby the lactones and ketonic esters are converted into the sodium salts of the corresponding ketonic acids, whilst the unsaturated hydroxy-esters remain practically unchanged. The results thus obtained were as follows, the value first given being the percentage of the product formed by 1 : 2-addition : methyl α-bromoacetate, 100%, 0% ; methyl α-bromopropionate, 55%, 45% ; methyl α-bromobutyrate, 50%, 50% ; methyl α-bromo*iso*butyrate and methyl bromomalonate, 0%, 100%.

In several cases no reaction occurred when the bromo-esters were heated with zinc and the unsaturated ketone in benzene solution. The reaction is, however, readily induced by the addition of a small quantity of the copper salt of ethyl acetoacetate, or of other copper compounds which are soluble in benzene.

The action of zinc on methyl bromoacetate and phenyl styryl ketone has been re-investigated, and the product, after removal of methyl β-hydroxy-β-phenyl-α-benzylidenebutyrate, carefully examined for methyl benzoylphenylbutyrate, which would be formed by a 1 : 4-addition, but no evidence of its presence could be obtained. Methyl β-hydroxy-β-phenyl-γ-benzylidenebutyrate decomposes below 150° into methyl acetate and phenyl styryl ketone ; a similar decomposition into potassium acetate and phenyl styryl ketone takes place on treating the ester with alcoholic potassium hydroxide. When hydrolysed with aqueous sodium carbonate, it yields the corresponding acid, $CHPh\!:\!CH{\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2H$, which crystallises in colourless needles,

147° (decomp.). When warmed with a small quantity of hydrochloric the hydroxy-ester is converted into a viscid oil, which is hydrolysed alcoholic potassium hydroxide to *β-phenylcinnamylideneacetic acid*, Ph:CH·CPh:CH·CO_2H; this forms pale yellow, slender needles, 145—146°.

The product obtained by the interaction of zinc, ethyl α-bromopropionate, and phenyl styryl ketone in benzene solution, when decomposed with hydrochloric acid and heated with aqueous sodium carbonate, yields a mixture of two stereoisomeric *ethyl β-hydroxy-β-phenyl-γ-benzylidene-α-methylbutyrates*,

CHPh:CH·CPh(OH)·CHMe·CO_2H,

which may be separated by repeated crystallisation from methyl alcohol. The less soluble isomeride crystallises in slender needles, m. p. 107°, instantly decolorises bromine at the ordinary temperature, and decomposes above its m. p. into ethyl propionate and phenyl styryl ketone. When warmed with alcoholic potassium hydroxide, it yields phenyl styryl ketone and potassium propionate. The stereoisomeride, which is produced only in small quantity, separates from alcohol in large, transparent prisms, m. p. 81°, and resembles the preceding compound in its chemical properties.

The alkaline solution from which the above esters were separated yields on acidification two stereoisomeric *γ-benzoyl-β-phenyl-α-methylbutyric acids*, CH_2Bz·CHPh·CHMe·CO_2H, which are separated by crystallisation from ether and light petroleum. Of these isomerides, the one obtained in larger quantity crystallises in slender, feathery needles, m. p. 149°, and yield a *methyl* ester crystallising in needles, m. p. , the *ethyl* ester has m. p. 41°. The stereoisomeric acid forms slender needles, m. p. 105°.

The product obtained by the action of zinc on methyl α-bromobutyrate and phenyl styryl ketone in benzene solution when decomposed with acid yields *methyl β-hydroxy-β-phenyl-γ-benzylidene-α-ethylbutyrate*,

CHPh:CH·CPh(OH)·CHEt·CO_2Me,

which crystallises in needles, m. p. 117°, and, when heated above its m. p., is resolved into methyl butyrate and phenyl styryl ketone. Decomposition of the product with aqueous sodium carbonate yields *γ-benzoyl-β-phenyl-α-ethylbutyric acid*, CH_2Bz·CHPh·CHEt·CO_2H, which crystallises in needles, m. p. 181°, and yields a *methyl* ester, m. p. 95°.

The *lactone*, $CHPh<\begin{matrix}CH{:}CPh\\CMe_2\cdot CO\end{matrix}>O$, obtained by the action of zinc on ethyl α-bromo*iso*butyrate and phenyl styryl ketone, forms long, colourless needles, m. p. 97°, and is readily hydrolysed by alcoholic potassium hydroxide to *γ-benzoyl-β-phenyl-αα-dimethylbutyric acid*, CH_2Bz·CHPh·CMe_2·CO_2H, which crystallises in slender, white needles, m. p. 159—160°. The lactone is accompanied by the *ethyl* ester of the last-mentioned acid; this has m. p. 83°, and has also been prepared from the lactone and corresponding acid; the *methyl* ester has m. p. 92°.

γ-Bromo-γ-benzoyl-β-phenyl-αα-dimethylbutyric acid,

CHBzBr·CHPh·CMe_2·CO_2H,

prepared by brominating the preceding ketonic acid in chloroform or

carbon tetrachloride solution, forms colourless needles, m. p. [illegible] (decomp.); the *methyl* ester, m. p. 125°, and *ethyl* ester, m. p. [illegible], were prepared in a similar manner. When treated with [illegible] sodium carbonate the bromo-acid yields two stereoisomeric γ-[illegible] *β-phenyl-αα-dimethyl-γ-butyrolactones*,

$$\begin{array}{l} CHPh—CHBz \\ CMe_2\cdot CO\cdot O \end{array}$$

, which may be separated by extraction with methyl alcohol. The more [illegible] modification forms needles, m. p. 113°; the stereoisomeride separates from acetone in needles, having m. p. 173°. When dissolved in [illegible] alcoholic potassium hydroxide and the resulting solution immediately acidified, both isomerides yield a mixture of two stereoisomeric *γ-hydroxy-γ-benzoyl-β-phenyl-αα-dimethylbutyric acids*,

$$OH\cdot CHBz\cdot CHPh\cdot CMe_2\cdot CO_2H.$$

The less fusible of these acids loses water so readily that it could [illegible] be obtained free from the lactone of m. p. 173°. The stereoisomeric acid, which forms the major portion of the mixture, separates from ether in needles, m. p. 126° (decomp.); when heated for several hours at 120°, it loses water and is converted into the lactone of m. p. 113°.

Methyl bromomalonate, prepared by the addition of the calculated amount of bromine to methyl malonate, is a colourless, mobile liquid, b. p. 145°/22 mm. It reacts with zinc and phenyl styryl ketone in benzene solution, yielding *methyl β-benzoyl-α-phenylethylmalonate*, $CH_2Bz\cdot CHPh\cdot CH(CO_2Me_2)_2$. The latter compound crystallises in large, colourless needles, m. p. 107°, and is hydrolysed by alcoholic potassium hydroxide to the corresponding acid (Vorländer, Abstr., 1897, i, 286), which loses carbon dioxide at 170°, yielding γ-benzoyl-β-phenylbutyric acid, m. p. 156°. The preceding ester is accompanied by a viscid liquid, which appears to be a lactonic ester [illegible] hydrolysed with alcoholic potassium hydroxide, this yields the same acid as that obtained by the hydrolysis of methyl β-benzoyl-α-phenylethylmalonate.

F. B.

Crystallographic Study of Potassium *p*-Hydroxybenzoate.

ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 53—54). This substance, prepared by Comanducci and Marcello (Abstr., [illegible] i, 485), forms transparent, colourless crystals belonging to the [illegible] system [$a:b:c=0.6471:1:1.7936$].

R. V. S.

o-Nitrophenylglyoxylic Acid.

GUSTAV HELLER [with FRIEDRICH FRANTZ and HEINRICH JÜRGENS] (*Ber.*, 1911, 44, 2418—[illegible]). *o*-Nitrophenylglyoxylic acid (compare Claisen and Shadwell, *Ber.*, [illegible] 12, 350) is conveniently prepared by oxidation of *o*-nitromandelic acid (Heller and Amberger, Abstr., 1904, i, 416) with alkaline permanganate. It crystallises in colourless, obliquely cut prisms, m. p. 156—157°.

The *ethyl* ester forms crystals, m. p. 43—44·5°.

The acid is reduced by zinc dust and ammonia to anthroxanic acid; the ester when reduced by stannous chloride and hydrochloric acid is converted into *ethyl anthroxanate*; this crystallises in long, [illegible] needles, m. p. 64—65°.

Methyl anthroxanate forms crystalline bunches, m. p. 70°.

E. F. A.

Keto-enolic Tautomerism. V. Desmotropy of Methyl Benzoylacetate. KURT H. MEYER (*Ber.*, 1911, 44, 2729—2732).—Methyl and ethyl benzoylacetate contain respectively 16·7% and ...% of enolic modification at the ordinary temperature.

If the methyl ester is dissolved in sodium hydroxide solution and precipitated by dilute sulphuric acid, both strongly cooled, the free enol separates as an oil which solidifies when vigorously shaken; the solid can be dried in an absolute vacuum, but it is soon converted into an equilibrium mixture of enol and ketone. This behaviour is similar to that of isophenylnitromethane. The enolic form or methyl β-hydroxycinnamate melts indefinitely at 30—40°, and solidifies again when rapidly cooled. The alcoholic solution is coloured intensely reddish-violet by ferric chloride, and also reacts quickly with *anti-p*-nitrobenzenediazonium hydroxide. The crystalline enol, after two hours' drying, contained ...% of the enolic form. In a state of equilibrium at 20°, the ester contained 14% of enol in acetic acid, 21% in alcohol, 56% in carbon disulphide, and 69% in hexane. These numbers are similar to those obtained with ethyl acetoacetate.

The values of the velocity constants at 0° in absolute alcohol are k_1 (ketonisation) = 0·10 and k_2 (enolisation) = 0·04. At the boiling point the alcoholic solution contains only about one-half as much enol as at 0°.

Unlike the equilibrium of ethyl acetoacetate, that of methyl benzoylacetate exhibits a distinct temperature-coefficient, the equilibrium being displaced towards the ketone by rise of temperature; the same is the case with acetylacetone, so that the independence of the equilibrium on the temperature is a constitutive property of ethyl acetoacetate. T. H. P.

Preparation of *m*-Hydroxy-β-phenylpropionic Acid Alkyl Ethers and their Salts. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234852).—*m-Ethoxy-β-phenylpropionic acid*, m. p. 52—53°, b. p. 205°/20 mm., can be prepared (1) by heating *m*-hydroxy-β-phenylpropionic acid with ethyl bromide and sodium hydroxide in alcoholic solution at 120°; (2) by reducing *m*-ethoxycinnamic acid with sodium amalgam; or (3) by diazotising *m*-amino-β-phenylpropionic acid in an anhydrous solvent, isolating the diazonium sulphate with ether, and subsequently boiling it with absolute alcohol; the *sodium* salt forms an odourless powder.

m-Propoxy-β-phenylpropionic acid has m. p. 56—57° and b. p. 203—204°/15 mm. These compounds have antipyretic and antirheumatic properties. F. M. G. M.

New Reactions of Cyanogen and Acyl Cyanides. DANIEL VORLÄNDER [and, in part, A. FRIEDBERG, CH. VAN DER MERVE, ROSENTHAL, M. E. HUTH, and M. VON BODECKER] (*Ber.*, 1911, 44, 2455—2476).—The interaction of cyanogen with benzene and its homologues, or with phenolic ethers, yields acyl cyanides, R·CO·CN, nitriles, R·CN, and diketones, R·CO·CO·R, together with more complex substances, the constitution of which has not been determined.

When cyanogen is passed into a mixture of benzene and aluminium chloride for one hour at the ordinary temperature, and the product decomposed with cold dilute hydrochloric acid, benzoyl cyanide is produced. If the mixture is boiled and the passage of cyanogen continued for two hours, the benzoyl cyanide is accompanied by benzonitrile (compare Desgrez, Abstr., 1896, i, 419). The product of the reaction always contains a certain amount of a tarry substance, which, on decomposition with acids, yields benzil. The latter compound forms the main product when a mixture of benzene and aluminium chloride is saturated with cyanogen and allowed to remain at the ordinary temperature for three days. In addition to the above compounds, several other substances are formed in the reaction, one of these being a blue dye, m. p. 145—148°.

With respect to the mechanism of the reaction, it is considered that the first stage consists in the formation of an imino-nitrile (I), which decomposes into benzonitrile and hydrogen cyanide, and on treatment with acids yields benzoyl cyanide, thus:

$$C_6H_6 + C_2N_2 \longrightarrow \text{(I) } CN\cdot CPh\colon NH \longrightarrow CN\cdot COPh\,;$$

the formation of benzil is due to the decomposition of a di-imino-compound (II), produced by the further condensation of the imino-nitrile with benzene:

$$CN\cdot CPh\colon NH + C_6H_6 = \text{(II) } NH\colon CPh\cdot CPh\colon NH.$$

The interaction of cyanogen, toluene, and aluminium chloride, under conditions similar to those given in the case of benzene, results in the formation of *p*-toluonitrile, *p*-toluic acid, *pp'*-dimethylbenzil, and *p*-methylbenzoyl cyanide (Söderbaum, Abstr., 1893, i, 159).

With ethylbenzene the product consists of p-*ethylbenzonitrile* and *p*-ethylbenzoic acid, together with p-*ethylbenzoyl cyanide*, which could not be isolated, and was therefore identified by conversion into *p*-ethylbenzanilide, m. p. 121°.

The only substance which could be identified in the product obtained from cyanogen and diphenyl was p-*phenylbenzoyl cyanide*.

The action of cyanogen and hydrogen chloride on a solution of phenetole in carbon disulphide in the presence of aluminium chloride yields p-*ethoxybenzoyl cyanide*, which has m. p. 43°, and is more readily prepared by heating *p*-ethoxybenzoyl chloride with mercuric cyanide at 125—130°; it gives a green, and finally blue, solution with strong sulphuric acid, and is decomposed by boiling with dilute hydrochloric acid into *p*-ethoxybenzoic acid and hydrogen cyanide; with aniline it yields *p*-ethoxybenzanilide (Leuckart, Abstr., 1890, 759).

p-*Ethoxyphenylglyoxylic acid*, obtained by the action of fuming hydrochloric acid on the preceding nitrile, crystallises with water in colourless prisms, m. p. 52°; the anhydrous acid is obtained by crystallisation from benzene, and has m. p. 125° (decomp.): it yields a *phenylhydrazone*, $C_{16}H_{16}O_3N_2$, long, yellow needles, m. p. 153° (decomp.), and an *azine*, crystallising in light yellow needles, which have m. p. 173—176°, and simultaneously lose carbon dioxide with the formation of *pp'*-diethoxybenzalazine; the *oxime* has m. p. 152—154° (decomp.).

pp'-*Diethoxybenzil*, $C_{18}H_{18}O_4$, prepared by the action of cyanogen and hydrogen chloride on a carbon disulphide solution of phenetole in the presence of aluminium chloride for three to four days, crystallises [illegible]

ivory-white, microscopic prisms, m. p. 149°, and gives a red coloration with concentrated sulphuric acid. It yields an *osazone*, crystallising in small, yellow plates, m. p. 171°, and is converted by alcoholic potassium hydroxide into pp′-*diethoxybenzilic acid*, which forms narrow prisms, m. p. 202°, with previous darkening.

p-Methoxybenzoyl cyanide, obtained from anisole in the usual manner, crystallises in colourless needles, m. p. 60°; Mauthner (Abstr., 1909, i, 160) gives 63—64°. It may also be prepared by the interaction of anisoyl chloride and mercuric cyanide; when warmed with acids or alkalis it yields anisic acid.

In view of the above-mentioned formation of benzil from the intermediate product, NH:CPh·CN, it was anticipated that the closely related benzoyl cyanide would condense with benzene to form benzil in a similar manner.

It was, however, found that benzoyl cyanide and benzene react at the ordinary temperature in the presence of aluminium chloride and hydrogen chloride, yielding 9-cyanofluorene (Wislicenus and Russ, Abstr., 1910, i, 839), which is converted by heating with fuming hydrochloric or hydriodic acid into 9-fluorenecarboxylic acid. On the other hand, when a mixture of benzene, benzoyl cyanide, and aluminium chloride is heated in carbon disulphide solution, triphenylacetonitrile (E. and O. Fischer, Abstr., 1879, 326, 385) is produced, thus: $CN\cdot COPh + 2C_6H_6 \longrightarrow CPh_3\cdot CN + H_2O$.

A number of substituted derivatives of triphenylacetonitrile has been prepared in a similar manner.

Phenyldi-p-tolylacetonitrile, $C_{22}H_{19}N$, obtained from benzoyl cyanide and toluene, crystallises in apparently monoclinic prisms, m. p. 132—133°, and is converted by the action of sodium on its alcoholic solution into phenyldi-*p*-tolylmethane (Kliegl, Abstr., 1905, i, 186); it may also be prepared by heating ω-chlorophenyldi-*p*-tolylmethane (Gomberg, Abstr., 1904, i, 489) with mercuric cyanide.

4:4′-*Diethyltriphenylacetonitrile*, $C_{24}H_{23}N$, prepared from ethylbenzene and benzoylcyanide, crystallises in colourless plates, m. p. 111—112°.

4:4′-*Dimethoxytriphenylacetonitrile*, $C_{22}H_{19}O_2N$, obtained from anisole, crystallises in short, colourless, rods, m. p. 98°; it is also obtained in small yield by the interaction of ω-chloro-4:4′-dimethoxytriphenylmethane and mercuric cyanide. When reduced with sodium in alcoholic solution, it yields 4:4′-dimethoxytriphenylmethane (Baeyer and Villiger, Abstr., 1902, i, 380).

4:4′-*Dihydroxytriphenylacetonitrile*, $C_{20}H_{15}O_2N$, prepared by boiling the preceding nitrile with hydriodic acid, forms colourless, hexagonal leaflets, m. p. 202°; it is converted by the action of methyl sulphate in alkaline solution into the original nitrile; the *diacetyl* derivative crystallises in colourless leaflets, m. p. 130°. When boiled with phosphorus and hydriodic acid, 4:4′-dimethoxytriphenylacetonitrile yields -hydroxydiphenylacetic acid (Bistrzycki and Flatau, Abstr., 1897, i, 90), which forms an *ethyl* ester, crystallising in stellar aggregates of prisms, m. p. 92°; the *methyl* ester is an oil.

4-*Methoxytriphenylacetonitrile*, prepared from anisoyl cyanide and benzene, crystallises in colourless plates or white needles, m. p. 137°.

4 : 4′-*Diethoxytriphenylacetonitrile*, obtained from benzoyl cyanide and phenetole, forms short, pointed prisms, m. p. 120°; it is converted by heating with hydriodic acid into 4 : 4′-dihydroxytriphenylacetamide and 4-hydroxydiphenylacetic acid.

Cyanogen and sulphurous acid react slowly in aqueous solution, yielding hydrogen cyanide and sulphuric acid :

$$C_2N_2 + H_2SO_3 + H_2O = 2HCN + H_2SO_4.$$

F. B.

Condensation of *p*- and *o*-Methoxymandelonitriles with Phenols and Phenolic Ethers. AUGUSTIN BISTRZYCKI, J. PAULUS, and R. PERRIN (*Ber.*, 1911, **44**, 2596—2617).—The paper contains merely a description of the following substances, and has been published in consequence of Stoermer and Hildebrandt's recent work (this vol., i, 664).

o- and *p*-Methoxymandelonitriles condense like the corresponding acids with phenols or phenolic ethers in the presence of 73% sulphuric acid, yielding nitriles of the type $OMe·C_6H_4·CHAr·CN$; thus anisaldehydecyanohydrin (1 mol.) and phenol ($2\frac{1}{3}$ mols.) yield 4-*hydroxy-4′-methoxydiphenylacetonitrile*, $OMe·C_6H_4·CH(CN)·C_6H_4·OH$, prismatic needles, m. p. 175—176° (erroneously described by Stoermer and Hildebrandt as the lactone of *o*-hydroxyphenylanisylacetic acid), which forms an *acetyl* derivative, m. p. 85·5—86·5°, and is hydrolysed by boiling alcoholic potassium hydroxide, forming 4-*hydroxy-4′-methoxydiphenylacetic acid* (p-*hydroxyphenylanisylacetic acid*), m. p. 148·5—149·5°. This acid does not yield a lactone (consequently the hydroxyl group is assumed to be in the para-position), and evolves two-thirds of the theoretical quantity of carbon monoxide when heated with concentrated sulphuric acid at 170° (compare Bistrzycki and Siemiradzki, Abstr., 1908, i, 635). Anisaldehydecyanohydrin and *o*-cresol yield in a similar manner 4-*hydroxy-4′-methoxy-3-methyldiphenylacetonitrile*, m. p. 142—143° (*acetyl* derivative, m. p. 74·5—76°); the corresponding *acid*, m. p. 128—129°, loses two-thirds of the theoretical quantity of carbon monoxide with sulphuric acid at 100—120°. The lactone of *p*-hydroxytolylanisylacetic [2-hydroxy-4′-methoxy-5-methyldiphenylacetic] acid (Stoermer and Hildebrandt, *loc. cit.*) is hydrolysed by 5% potassium hydroxide to the corresponding *acid*, m. p. 110° (decomp.), which exhibits considerable stability for a γ-lactone. The lactone is converted into 2-*hydroxy-4′-methoxy-5-methyldiphenylacetamide*, decomp. 137·5°, by 25% aqueous ammonia and a little alcohol, and into the *hydrazide*, $OMe·C_6H_4·CH(CO·NH·NH_2)·C_6H_3Me·OH$, decomp. 182·5° (*benzylidene* derivative, m. p. 184°), in boiling alcohol by 50% aqueous hydrazine hydrate.

Anisaldehydecyanohydrin and catechol condense to form 3 : 4-*dihydroxy-4′-methoxydiphenylacetonitrile*,

$$OMe·C_6H_4·CH(CN)·C_6H_3(OH)_2,$$

m. p. 153·5—154·5°, darkening at 130° (*diacetate*, m. p. 77—78°), which develops a blue, and by warming a bluish-violet, coloration with concentrated sulphuric acid. Anisaldehydecyanohydrin and β-naphthol yield the *lactone* of 2-*hydroxy-α(?)-naphthyl-4-methoxyphenyl-*

...ic acid, $OMe\cdot C_6H_4\cdot CH<\genfrac{}{}{0pt}{}{CO}{C_{10}H_6}>O$, m. p. 145—146° (decomp.), ... prismatic needles.

Anisaldehydecyanohydrin condenses very readily with anisole to ... *dianisylacetonitrile* [4 : 4'-*dimethoxyphenylacetonitrile*], $CN\cdot CH(C_6H_4\cdot OMe)_2$, ... p. 154·5°. Dianisylacetic acid reacts readily with phosphorus pentachloride and phosphoryl chloride to form the *chloride*, $CH(C_6H_4\cdot OMe)_2\cdot COCl$, m. p. 58—61°. In a similar manner phenetole yields *anisylphenetylacetonitrile*, m. p. 87—88°, whilst veratrole yields 3 : 4 : 4'-*trimethoxydiphenylacetonitrile*, m. p. 96°, the corresponding *acid* having m. p. 154—155°.

o-Anisaldehydecyanohydrin (rhombic crystals, $a : b : c$ = ...62 : 1 : 0·462) condenses less readily than the para-isomeride with phenols, except *p*-cresol. The *lactone* of 2-*hydroxy*-2'-*methoxy*-5-*methyl*-*diphenylacetic acid*, $OMe\cdot C_6H_4\cdot CH<\genfrac{}{}{0pt}{}{CO}{C_6H_3Me}>O$, m. p. 136°, obtained directly from the cyanohydrin and *p*-cresol with 73% sulphuric acid on the water-bath, is hydrolysed to the *acid*, $C_{16}H_{16}O_4,H_2O$, m. p. ...°, by 6% potassium hydroxide, to the *amide*, $C_{16}H_{17}O_3N$, decomp. 177—178°, by alcoholic ammonia at 100°, to the *anilide*, m. p. 192—194°, by distillation with aniline, and to the *hydrazide*, m. p. ...4° (*benzylidene* derivative, m. p. 202°), by hydrazine hydrate.

The condensation of *o*-anisaldehydecyanohydrin and *o*-cresol yields a mixture of 4-*hydroxy*-2'-*methoxy*-3-*methyldiphenylacetamide* (prisms containing $C_2H_4O_2$, m. p. 130—131°, from acetic acid) and the lactone of 4-*hydroxy*-2'-*methoxy*-3-*methyldiphenylacetic acid*, m. p. 164°. The cyanohydrin and phenol likewise yield a mixture of the *lactone* of ...*hydroxy*-2'-*methoxydiphenylacetic acid*, m. p. 160—162°, and 4-*hydroxy*-...*methoxydiphenylacetamide*, m. p. 204—205°, which is hydrolysed ...ly slowly and incompletely by boiling concentrated potassium hydroxide.

C. S.

Diphenyl Derivatives. FRITZ MAYER (*Ber.*, 1911, **44**, 2298—2305).—The following substances were obtained in the course of attempts to synthesise pyrene by using Ullmann's method for the preparation of *s*-diphenyl derivatives (Abstr., 1901, i, 586).

2-Acetylaminoisophthalic acid, prepared by Noelting and Gachot's method (Abstr., 1906, i, 181), is best purified by heating with acetic anhydride, which gives rise to the corresponding *acetylanthranil*, m. p. 217—218°; the latter is readily re-converted into the acid by crystallisation from water. The acid softens at 195—200° and decomposes at 205—206°, and when warmed with diluted sulphuric acid yields 2-amino*iso*phthalic acid. The latter, on diazotisation and treatment with iodine in potassium iodide solution, gives 2-*iodo*-*isophthalic acid*, m. p. 205—222° (decomp.), with some of the corresponding hydroxy-acid, from which it is best separated by conversion into the *methyl* ester, m. p. 50°, long, colourless needles. The latter, when heated with copper powder at 140—150°, yields *diphenyl*-2 : 6 : 2' : 6'-*tetracarboxylic acid*, iridescent leaflets, melting above 350°, in the form of the *tetramethyl* ester, m. p. 125—126°, which crystallises

in colourless needles. The corresponding *acid chloride*, $C_{16}H_{8}O_{2}Cl_{2}$, m. p. 189—190°, obtained as a brittle mass by precipitation with light petroleum from benzene, does not yield pyrene on reduction with the usual agents, and when heated with copper gives an amorphous, red substance.

2-*Iodo*-m-*toluic acid*, m. p. 145—146°, prepared from the corresponding methyl aminotoluate (Müller, Abstr., 1909, i, 156) by diazotising, adding potassium iodide, and hydrolysing the methyl ester, b. p. 280—290°, so obtained, crystallises in needles from benzene or methyl alcohol. When heated with copper powder at 220°, it yields 2 : 2′-*dimethyldiphenyl*-6 : 6′-*dicarboxylic acid*, which crystallises from ether on addition of light petroleum, sinters strongly, and finally melts at 230°. The yield is small.

Methyl o-*iodocinnamate*, m. p. 65°, crystallises in silky, yellow needles, and does not yield pyrene when heated with copper powder.

o-Iodobenzaldehyde may be readily identified by condensing it with aniline, when it yields o-*iodobenzylideneanilene*, m. p. 75—76°, crystallising from methyl alcohol in colourless needles. When heated with copper powder at 210—220°, *o*-iodobenzaldehyde furnishes 2 : 2′-*dialdehydodiphenyl* as a viscous, brown oil with an odour similar to that of benzaldehyde; the *dioxime*, m. p. 175—176°, crystallises from methyl alcohol in yellow needles. The dialdehyde, when heated with acetic anhydride and sodium acetate, is converted into *diphenyl*-2 : 2′-*diacrylic acid*, m. p. 286° (decomp.), which crystallises from acetic acid, yields diphenic acid on oxidation with dilute alkaline permanganate, and when distilled alone or with lime, lead oxide, or zinc dust, gives an oily substance which slowly deposits a small amount of crystalline matter from which a *picrate*, m. p. 140°, can be obtained. T. A. H.

Simultaneous Reduction and Oxidation by Catalysis. NICOLAI ZELINSKY and NIKOLAUS GLINKA (*Ber.*, 1911, 44, 2305—2311*).—Methyl Δ^{1}-tetrahydroterephthalate, dissolved in dry ether, when treated with palladium black in presence of a current of hydrogen at atmospheric temperature furnishes a mixture of methyl terephthalate and methyl *cis*-hexahydroterephthalate. The same change takes place, but more slowly, with platinum black. The oxidation is not due to oxygen occluded by palladium, since it does not occur in absence of hydrogen. The mechanism of the reaction may be that the tetrahydroterephthalate is immediately reduced in part by the palladium in virtue of hydrogen occluded by the latter, the hydrogen thus lost by the palladium being recovered from the residual tetrahydroterephthalate, so that a re-distribution of the hydrogen in 3 mols. of the tetrahydroterephthalate occurs thus: $3C_{10}H_{14}O_4 = 2C_{10}H_{16}O_4 + C_{10}H_{10}O_4$; or, as suggested by Bach (Abstr., 1910, ii, 31), a labile palladium perhydride may be formed, which reacts with an oxyperhydride, OH_4, momentarily formed, in which, under the influence of palladium perhydride, the normal affinity of oxygen in the molecule of water is so distributed as to hold 4H in place of 2H. The existence of such an intermediate product would explain (1) the simultaneous occurrence of oxidation and reduction as

* and *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1084—1091.

... instance; (2) Ipatieff's observation that in catalytic reduction at ... pressures the presence of oxygen favours the action, and (3) that Sabatier's nickel reduction method, nickel prepared at 200—250°, which temperature it may still contain oxygen, gives the best results. The palladium black used in these experiments was obtained by adding first formic acid and then alkali to an aqueous solution of palladium ammonium chloride. T. A. H.

Preparation of Dichloro-o-carboxyphenylthiolacetic Acid. ... & Co (D.R.-P. 234375).—When the di- or tri-halogenated carboxyphenylthiolacetic acid neutral esters are treated with sodium hydroxide, they yield the corresponding halogenated oxythionaphthen-carboxylic acid esters, which are then hydrolysed and the resulting product oxidised to dyes.

Dichloro-o-carboxyphenylthiolacetic acid, $CO_2H\cdot C_6H_2Cl_2\cdot S\cdot CH_2\cdot CO_2H$, glistening, colourless needles, was prepared as follows: Aceto-o-toluidide was dichlorinated, oxidised with potassium permanganate to dichloro-acetylanthranilic acid, the acetyl group eliminated, and the dichloro-anthranilic acid so obtained, diazotised and converted into either a dichloro-o-thiolbenzoic acid or a xanthate derivative, which on subsequent treatment with chloroacetic acid yielded the foregoing acid. Esterification was carried out in the usual way, and the ring subsequently closed by heating at 40—50° with concentrated sodium hydroxide, yielding *ethyl dichloro-3-oxy-(1)-thionaphthencarboxylate*, which was not isolated but hydrolysed by dilution and prolonged boiling. Subsequent oxidation with potassium ferricyanide (or air) furnished a dye which was isolated as a dark violet powder. F. M. G. M.

Action of Organo-magnesium Compounds on 4-Methoxy-phthalic Anhydride. Hugo Bauer (*Arch. Pharm.*, 1911, **249**, 450—453).—It has been shown previously (Abstr., 1908, i, 274) that the nitro-group in nitrodiethylphthalide (Abstr., 1904, i, 417) probably occupies position 5, and to confirm this an attempt was made to synthesise 5-methoxydiethylphthalide, which was prepared from the nitro-compound as described already (Abstr., 1908, i, 274). By the action of magnesium ethyl bromide on 4-methoxyphthalic anhydride, either 4- or 5-methoxydiethylphthalide might be formed, and trial proved that the former only was produced.

4-Methoxydiethylphthalide, $OMe\cdot C_6H_3<\substack{CEt_2\\ CO}>O$, m. p. 86—87°, crystallises from dilute alcohol in colourless prisms. On fusion with potassium hydroxide, it furnishes anisic acid, and on nitration gives only a *mononitro*-derivative, m. p. 117°, which crystallises from alcohol in faintly yellow needles. On reduction with iron and acetic acid at 100°, this gives the corresponding *amino*-compound, m. p. 163°, which crystallises from dilute alcohol in colourless leaflets or prisms. It fluoresces blue in alcohol solution. T. A. H.

Action of Organo-magnesium Compounds on Homophthalic Anhydride. Hugo Bauer and Ewald Wölz (*Arch. Pharm.*, 1911, **249**, 454—458. Compare Abstr., 1904, i, 417; 1905, i, 210; 1909, i, 585, and preceding abstract).—The previous work (*loc. cit.*)

has shown that the normal action between organo-magnesium compounds and dicarboxylic anhydrides gives rise to dialkylphthalides, but in certain cases other reactions occur, such as the formation of o-diketones or the production of monoalkylphthalides. This condensation has therefore been further investigated with homophthalic anhydride in place of phthalic anhydride. The former may give rise to dialkyl derivatives of either type represented by the formulæ:

$$C_6H_4<\begin{matrix}CR_2\cdot O\\ CH_2\cdot CO\end{matrix} \quad \text{or} \quad C_6H_4<\begin{matrix}CH_2\cdot CR_2\\ CO-O\end{matrix}.$$

The former type should yield on fusion with potassium hydroxide, and assuming R to be Me, acetone and phenylacetic acid, whilst the second should give acetone and o-toluic acid. Application of this reaction to the condensation products gave unexpected results, so that at present constitutional formulæ cannot be assigned to them.

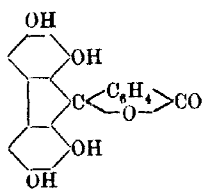
Dimethylhomophthalide, $C_{11}H_{12}O_2$, m. p. 94—95°, obtained by condensing magnesium methyl iodide with homophthalic anhydride and treating the product with dilute acid, crystallises from hot ether in slender, colourless needles, dissolves in warm alkalis, and is reprecipitated by acids, does not react with hydroxylamine or ammonia, and fluoresces green when warmed with sulphuric acid.

Diphenylhomophthalide, $C_{21}H_{16}O_2$, m. p. 160—161°, similarly prepared, crystallises from alcohol, and resembles the foregoing substance in properties, but gives an orange-red to brownish-red coloration with sulphuric acid.

Dibenzylhomophthalide, $C_{23}H_{20}O_2$, m. p. 163—164°, crystallises from alcohol, and gives a wine-red coloration with sulphuric acid.

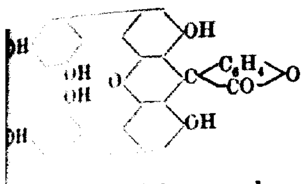
T. A. H.

Phthaleins of 3:5:3′:5′-Diresorcinol (3:5:3′:5′-Tetrahydroxydiphenyl). Richard Meyer and Karl Meyer (*Ber.*, 1911, 44, 2678—2684).—The soluble phthalein obtained by Benedikt and Julius (Abstr., 1884, 1139; compare also Link, *ibid.*, 1881, 95) by the condensation of phthalic anhydride and 3:5:3′:5′-tetrahydroxydiphenyl in the presence of concentrated sulphuric acid has, according to the authors, the annexed constitution.



When warmed with acetic anhydride and a little sulphuric acid, it yields a *tetra-acetate*, which forms long, flat, rhomb-shaped crystals, m. p. 237—238°; the *tetrabenzoate* crystallises in stout, prismatic needles, m. p. 180—181°. The *tetramethyl ether*, $C_{20}H_8O_2(OMe)_4$, obtained by the action of methyl sulphate in alkaline solution, forms colourless needles; the *tetraethyl ether*, prepared by alkylating the phthalein either with ethyl iodide and sodium ethoxide in alcoholic solution, or by means of ethyl sulphate in alkaline solution, crystallises in flat needles or leaflets, m. p. 223°. When brominated in glacial acetic acid solution the phthalein yields a *tribromo*-derivative, $C_{20}H_9O_6Br_3$, crystallising in slender needles.

The insoluble phthalein, obtained by Benedikt and Julius (*loc. cit.*), is best prepared by the condensation of 1 mol. of phthalic anhydride with 2 mols. of 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in the presence of concentrated sulphuric acid at 120°. It has no m. p., dissolves in alkalis with a blue coloration, and is considered to be a hexahydroxydiphenylfluoran of the annexed constitution.



It yields a *hexabenzoate*, crystallising in broad leaves, m. p. 245—250°; the *hexaethyl ether*, prepared by means of ethyl sulphate, crystallises in needles, m. p. 234—236°.

4 : 4′-(or 2 : 2′-)-*Bisbenzeneazo*-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl*,

$$NPh{:}N{\cdot}C_6H_2(OH)_2{\cdot}C_6H_2(OH)_2{\cdot}N{:}NPh,$$

obtained by the combination of benzenediazonium chloride and 3 : 5 : 3′ : 5′-tetrahydroxydiphenyl in alkaline solution, crystallises in stout, red needles having a steel-blue lustre.

4 : 4′-(or 2 : 2′-)-*Bis*-p-*tolueneazo*-3 : 5 : 3′ : 5′-*tetrahydroxydiphenyl*,

$$C_{12}H_8O_4(N_2{\cdot}C_7H_7)_2,$$

prepared in a similar manner, forms slender, red needles. F. B.

Synthesis of Chrysene. Erich Beschke [with Mariam Winogradowa-Israel and Georg Kohres] (*Annalen*, 1911, 384, 143—172).—The interaction of benzil, ethyl bromoacetate, and zinc in boiling benzene leads to the formation of the racemic and meso-modifications, m. p. 37 and 168° respectively, of *ethyl βγ-dihydroxy-βγ-diphenyladipate*, $CO_2Et{\cdot}CH_2{\cdot}CPh(OH){\cdot}CPh(OH){\cdot}CH_2{\cdot}CO_2Et$, which are separated by the insolubility of the latter in cold benzene. When boiled with acetic and concentrated hydrochloric acids, or heated above its m. p., the racemic modification is easily converted into the *di-lactone*, $CO<\begin{matrix}O—CPh{\cdot}CH_2\\CH_2{\cdot}CPh—O\end{matrix}>CO$, m. p. 194°, which is being examined.

The meso-modification forms a *diacetyl* derivative, m. p. 171°, and is hydrolysed by boiling 10% sodium hydroxide, yielding the *sodium* salt, $C_{18}H_{16}O_6Na_2,10H_2O$, from which a stable, sparingly soluble *silver* salt, $C_{18}H_{16}O_6Ag_2,3H_2O$, has been prepared. The anhydrous silver salt is converted into silver, carbon dioxide, and acetophenone by distillation, and regenerates the meso-ester with ethyl iodide. *βγ-Dihydroxy-βγ-diphenyladipic acid*, m. p. 205°, obtained from the sodium salt and dilute acetic acid, is converted by alcoholic hydrogen chloride, not into the original meso-ester, but into *ethyl β-hydroxy-βγ-diphenylbutyrolactone-γ-acetate* [3-*hydroxy*-5-*keto*-2 : 3-*diphenyltetrahydrofuran*-2-*acetate*], $CO_2Et{\cdot}CH_2{\cdot}CPh<\begin{matrix}CPh(OH){\cdot}CH_2\\O\end{matrix}>CO$, m. p. 138°, which is also obtained by adding a little concentrated hydrochloric acid to a boiling concentrated solution of the meso-ester in glacial acetic acid. β-*Hydroxy-βγ-diphenylbutyrolactone-γ-acetic acid*, $C_{18}H_{16}O_5$, m. p. 179°, is obtained by the action of acetic acid and a mineral acid on its ethyl

ester or on **βγ-dihydroxy-βγ-diphenyladipic acid**, but by too prolonged action the former method yields *βγ-diphenylcrotonolactone-γ-acetic* [*5-keto-2 : 3-diphenyl-2 : 5-dihydrofuran-2-acetic*] *acid*,

$$CO_2H\cdot CH_2\cdot CPh\Big<\begin{matrix}CPh{:}CH\\ \;|\\ O\text{——}CO\end{matrix},$$

m. p. 184°. This acid, however, in the form of its *ethyl ester*, m. p. 94°, is more easily obtained by treating the above-mentioned meso-ester in acetic anhydride with concentrated sulphuric acid below 40—50°.

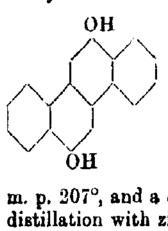
When ethyl βγ-diphenylcrotonolactone-γ-acetate is treated with boiling alcoholic sodium hydroxide (not in excess), the sodium salts of two acids are obtained. One of these acids is the *monoethyl* ester of βγ-diphenylmuconic acid, $CO_2H\cdot CH{:}CPh\cdot CPh{:}CH\cdot CO_2Et$, m. p. 140°, which lactonises to the original ester when boiled with acetic acid. The other acid is βγ-diphenylmuconic acid, which, however, cannot be isolated, since it at once changes to βγ-diphenylcrotonolactone-γ-acetic acid when liberated from its sodium salt. *Diethyl βγ-diphenylmuconate*, m. p. 72°, obtained from the silver salt of either of the two acids and ethyl iodide, reacts with bromine in chloroform in sunlight to form a *substance*, $C_{20}H_{17}O_4Br$, m. p. 143°, which probably has the constitution

$$CO_2Et\cdot CHBr\cdot CPh\Big<\begin{matrix}CPh{:}CH\\ \;|\\ O\text{——}CO\end{matrix}.$$

When aqueous sodium βγ-diphenylmuconate is treated with iodine in potassium iodide and the solution is acidified after prolonged keeping, *βγ-diphenylcrotonolactone-γ-iodoacetic acid*,

$$CO_2H\cdot CHI\cdot CPh\Big<\begin{matrix}CPh{:}CH\\ \;|\\ O\text{——}CO\end{matrix},$$

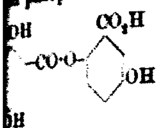
m. p. 217°, is obtained, which is reduced by zinc and acetic acid to *βγ-diphenyl-αδ-dihydromuconic acid*, $CO_2H\cdot CH_2\cdot CPh{:}CPh\cdot CH_2\cdot CO_2H$, m. p. 297°. This acid is best obtained by reducing sodium diphenylmuconate with sodium amalgam, whereby an *acidic* by-product, $C_{18}H_{16}O_4$, m. p. 195° (*ethyl* ester, m. p. 56°), is also formed, which is easily soluble in alcohol. Diphenyldihydromuconic acid forms an *ethyl* ester, m. p. 86°, and is converted by acetic anhydride and concentrated sulphuric acid into the *di-acetate*, m. p. 246°, of 2 : 8-*dihydroxychrysene* (annexed constitution), which is itself obtained by hydrolysing the diacetate by trituration with cold concentrated sulphuric acid. 2 : 8-Dihydroxychrysene yields yellow solutions in alkalis (becoming blue in the air), forms a *diethyl ether*, m. p. 207°, and a *dibenzoate*, m. p. 280°, and is reduced to chrysene by distillation with zinc dust.



C. S.

Methylcarbonato-derivatives of Phenolcarboxylic Acids and their Use for Synthetic Operations. V. EMIL FISCHER and KARL FREUDENBERG (*Annalen*, 1911, **384**, 225—244. Compare Abstr., 1910, i, 265).—Didepsides of the more important di- and tri-hydroxybenzoic acids have been prepared on account of their relation to many natural products.

Dimethylcarbonatodigentisic acid, $C_{18}H_{14}O_{11}$, m. p. 166—167° rr.), colourless, flexible needles, is obtained by shaking a mixture 5-methyl-carbonato-2-hydroxybenzoic acid, dimethylaniline, benzene, d phosphorus trichloride for three days at the ordinary temperature; its alcoholic solution develops a deep red coloration with ferric chloride.



Digentisic acid (annexed constitution), m. p. 208—209° (corr.), is obtained by hydrolysing the preceding compound by *N*-ammonia at 18—20° in an atmosphere of hydrogen. In ntrast to gentisic acid, it precipitates dilute solutions of albumin or quinine acetate, and develops a transient, blue coloration with ferric loride. *Dimethylcarbonatodi-β-resorcylic acid*, $C_{18}H_{14}O_4$, m. p. 3—164° (corr.), obtained from 4-methylcarbonato-2-hydroxybenzoic id by a modification of the preceding process, yields by hydrolysis β-*resorcylic acid*, $C_6H_3(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 215° rr., decomp.).

3-*Methylcarbonato-4-hydroxybenzoic acid*, $CO_2Me\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, p. 176° (corr., decomp.), obtained by the partial hydrolysis of the methylcarbonatobenzoic acid (Abstr., 1908, i, 892), is converted to *iso*vanillic acid by treatment with diazomethane and subsequent drolysis. When treated in acetone with *N*-sodium hydroxide and 4-dimethylcarbonatobenzoyl chloride in an atmosphere of hydrogen, yields, after hydrolysis of the product, *diprotocatechuic acid*, $H_3(OH)_2\cdot CO\cdot O\cdot C_6H_3(OH)\cdot CO_2H$, m. p. 237—239° (corr., decomp.).

Digallic acid, $C_{14}H_{10}O_9$, m. p. 282° (corr., decomp.), is obtained in a milar manner to the preceding acid; it precipitates solutions of bumin and of quinine acetate, and develops the usual bluish-black loration with ferric chloride.

The following depsides have been prepared by similar methods. With KURT HOESCH.]—*Diferulic acid*, m. p. 241—242°; *di-o-umaric acid*, m. p. 188—190°; *di-β-hydroxynaphthoic acid*, m. p. 5°; 4-*feruloyloxybenzoic acid*, m. p. 233°; 4-α-*hydroxynaphthoyl-ybenzoic acid*, m. p. 246—247°. [With R. LEPSIUS.]—*Disyringic id*, m. p. 260°; *di-m-hydroxybenzoic acid*, m. p. 199°; 4-*syringoyl-ybenzoic acid*, m. p. 208°; *p-hydroxybenzoylsyringic acid*, m. p. 2—284°; 4-*m-hydroxybenzoyloxybenzoic acid*, m. p. 239—240°; *p-hydroxybenzoyloxybenzoic acid*, m. p. 254°.

C. S.

p-Cresolglycuronic Acid. CARL NEUBERG and E. KRETSCHMER *ochem. Zeitsch.*, 1911, **36**, 15—19).—Phenols excreted in the urine e never found in the free state, but as derivatives of glycuronic d sulphuric acids.

p-Cresol given to dogs was found to be excreted as a *p*-cresol rivative of glycuronic acid, $C_6H_9O_7\cdot O\cdot C_6H_4Me$, and as *p*-tolyl drogen sulphate.

A barium salt was isolated from the urine, which proved to be a ixed salt of these two acids.

W. J. Y.

Cherry-laurel Water and Solutions of Benzaldehyde and ydrocyanic Acid in Water. P. H. WIRTH (*Arch. Pharm.*, 1911, **9**, 382—407).—An investigation of the equilibrium point reached

in aqueous solutions of benzaldehyde, benzaldehydecyanohydrin, and hydrogen cyanide under various conditions of temperature, concentration, acidity, alkalinity, etc., with special reference to the determination of the usual composition of cherry-laurel water (compare Denigès, Abstr., 1894, ii, 165; Fromm, Abstr., 1898, i, 266). The following points are established: All three compounds co-exist in aqueous solution, and the same equilibrium is reached whether the cyanohydrin or its two components be initially added to water. With increasing concentration, the equilibrium point moves in the cyanohydrin direction, and vice versa. The cyanohydrin is progressively dissociated into its components with rise of temperature. Alkalis in small quantities accelerate the rate at which equilibrium is reached, and cause dissociation of the cyanohydrin, but even in presence of considerable quantities of alkali the cyanohydrin is never completely dissociated (compare Ultée, Abstr., 1906, i, 5, and Rosenthaler, Abstr., 1909, i, 623). Equilibrium is reached less quickly in presence of acids. Silver nitrate produces silver cyanide in these solutions in presence of alkali, and the whole of the hydrogen cyanide may be thus removed, but in presence of acids the equilibrium is more stable, except under the influence of change of temperature or concentration.

The toxicity of benzaldehydecyanohydrin is proportional to the amount of hydrocyanic acid it can yield on dissociation. T. A. H.

Hydrogenation of Hydroaromatic Compounds. Victor Skworzow (*J. pr. Chem.*, 1911, [ii], 84, 422—424).—The usual method of reduction when applied to hydroaromatic ketones either fails or give poor results. The author finds that the reduction may be effected quite easily, and with almost quantitative yield, by means of sodium and alcohol, if carried out under pressure in an autoclave. *l*-Menthone yields by this method a mixture of solid and liquid dextrorotatory menthols, whilst from *d*-pulegone a lævorotatory mixture was obtained. F. B.

Ketens. V. Reactivity of the Carbonyl Group. Hermann Staudinger and N. Kon (*Annalen*, 1911, 384, 38—135. Compare this vol., i, 462).—Previous experiments have shown that diphenylketen reacts with carbonyl compounds to form β-lactones or their products of decomposition, carbon dioxide and ethylene derivatives (Abstr., 1908, i, 410, 411; this vol., i, 459), and have demonstrated, although not conclusively, on account of complications introduced by side reactions, that the reactivity of the carbonyl group is strongly influenced by the neighbouring substituents (Abstr., 1910, i, 46). The present paper describes an exhaustive examination of this influence. The efficacy of the method of examination previously employed (Abstr., 1910, i, 46) has been tested by experiments with benzophenone or fluorenone, since with these ketones side reactions are not possible. It is found that with molecular quantities, 1 : 1 or 1 : 10, of the ketone and diphenylketen (in the form of the solid diphenylketen-quinoline) at 131°, the expressions $x/at(a-x)$ or $1/t.\log a/(a-x)$ respectively are approximately constant during the first hour; subsequently their value diminishes, probably owing to the gradual polymerisation of the diphenylketen

...line. (It has been found that extensive polymerisation of ...ylketen-quinoline occurs even at 131° in the presence of ... substances which catalytically accelerate the process. The ...ride does not react with carbonyl compounds.) Consequently, ... experiments with other carbonyl compounds, the amount of ... dioxide evolved at the end of the first hour is taken as ...sure of the reactivity of the carbonyl group, of course provided ... the approximate constancy, during this interval, of one or other ... the preceding expressions, according to the relative quantities of ... carbonyl compound and diphenylketen employed, has afforded ...ence that side-reactions have not occurred to an extent sufficient ...nullify the results.

The influence of a number of like substituents on different ...onyl-containing groups has been examined in order to compare the ...tivity of the carbonyl group in aldehydes, ketones, and acid ...ivatives. In the formula R·CO·R', R is (I) Ph, (II) $OMe{\cdot}C_6H_4{\cdot}$, ... $NMe_2{\cdot}C_6H_4{\cdot}$, (IV) CHPh:CH·, thus giving four series of ...nyl compounds. The figures in the following list give, for ...ferent R's, the percentage amount of the ketone which enters into ... reaction during the first hour: R' = CHPh:CH, I. 31·4, II. 32·2, ... 52·3, IV. 69·0; R' = H, I. 3·8, II. 17·8, III. 53·0, IV. 38·3; ...CN, I. 2·2, IV. 52·6; R' = Ph, I. 1·4, II. 4·2, III. 37·8, IV. 31·4; ...Me, I. 2·2, II. 4·9, III. 11·4, IV. 16·3; R' = NMe_2, I. 2·5, II. 2·5, ... 12·2, IV. 11·4; R' = NPh_2, I. 2·5, IV. 4·8; R' = OMe, I. 0·2, ...1, III. 4·0, IV. 1·3; R' = Cl, I. 0·2, II. 0·2, III. 1·6, IV. 4·0. ...fortunately, the results do not allow any definite conclusions to be ...awn as to the influence of R and R' on the activity of the carbonyl ...oup, because the k of a unimolecular or bimolecular reaction is only ...proximately constant when R = Ph or $OMe{\cdot}C_6H_4$, and not at all ...stant in the other two series. However, several points are clearly ...icated. Firstly, the reactivity of the carbonyl group is very ...ferently influenced by different R''s in the four series, but always ... the same direction. Secondly, the reactivity of the carbonyl group ... greatest in the neighbourhood of the styryl group and least in ... acid chlorides and esters. Finally, compounds containing the ...namoyl group are more reactive than those containing the benzoyl ...oup.

The authors show that the varying reactivity of the carbonyl group ...not be explained by steric influences or by an increase or decrease ... the basic character of the carbonyl group caused by the neighbour... groups, but attribute it to the varying degree of unsaturation of ... carbonyl group; the greater the unsaturation of the group, the ...ater is its reactivity with diphenylketen. This leads them to a ...uction which is emphasised throughout the paper. Since chromo...es are unsaturated groups, the more unsaturated the carbonyl ...oup the more chromophoric is its character. In their experiments ... authors have observed that the carbonyl group in a coloured ...pound is more unsaturated (that is, more reactive) than that in a ...ourless compound of similar structure; moreover, influences which ...ensify the colour of a carbonyl compound also increase the un...uration of the carbonyl group. A general review of these and of

previous experiments shows that quinones and unsaturated **ketones react most energetically with diphenylketen, then** come, in order **of decreasing reactivity, aldehydes, aromatic ketones,** and acid **derivatives; it is the first two classes of compounds which** are most **prone to exhibit colour.**

The reactivity of the carbonyl group in a series of compounds containing the cinnamoyl group cannot be compared by the amount of carbon dioxide evolved, because the reaction proceeds in two directions; thus diphenylketen and phenyl styryl ketone react:

$$\mathrm{CHPh{:}CH{\cdot}COPh + CPh_2{:}CO} \begin{cases} \nearrow \mathrm{CHPh{:}CH{\cdot}CPh{:}CPh_2 + CO_2} \\ \searrow \mathrm{CHPh}<\begin{matrix}\mathrm{CH{:}CPh}\\\mathrm{CPh_2{\cdot}CO}\end{matrix}>\mathrm{O} \end{cases}$$

(this δ-lactone was previously stated to be 3-benzoyl-1:1:2-triphenyl-4-*cyclo*butanone, Abstr., 1910, i, 46).

The great reactivity of the whole conjugated system in phenyl styryl ketone is very remarkable in contrast with the slight reactivity of benzaldehyde and of styrene with diphenylketen. In the conjugated system, $\overset{4}{\mathrm{C}}{:}\overset{3}{\mathrm{C}}{\cdot}\overset{2}{\mathrm{C}}{:}\overset{1}{\mathrm{O}}$, the addition of diphenylketen occurs the more in the position 1:4 the more the carbon atom 4 is rendered unsaturated by neighbouring substituents; addition in the position 1:2 predominates when the oxygen atom is rendered more unsaturated. In the "crossed" conjugate system, $\begin{matrix}\mathrm{C{:}C}\\\overset{}{\underset{4\ \ 3}{\mathrm{C{:}C}}}\end{matrix}>\underset{2}{\mathrm{C}}{:}\underset{1}{\mathrm{O}}$, the distribution of the residual affinity is such that the oxygen is particularly unsaturated, and consequently the addition of diphenylketen occurs very largely at the carbonyl group. For example, phenyl styryl ketone and diphenylketen react to the extent of 87% in the 1:2 position and [illegible] in 1:4, whilst in the case of distyryl ketone the values are 71 and [illegible] respectively.

It is found, in general, that compounds containing a conjugated system are more reactive than those with a simple double linking, and that substances with a "crossed" system of double linkings are particularly unsaturated. Here again a parallelism is to be observed between unsaturation and colour; substances containing a conjugated system are more coloured than similar substances which do not, the colour being especially intense when a "crossed" conjugate system is present.

A similar parallelism is observed in the case of pyrone and pyrone-quinone; pyrones react very slightly with diphenylketen, whilst the quinones exhibit the greatest reactivity.

One of the most important points in the paper is the examination of the influence of auxochromic groups on the reactivity of a carbonyl group. (The auxochrome must be present as OR or $\mathrm{NR_2}$, since diphenylketen attacks the hydroxyl or amino-group in preference to the carbonyl group.) A study of the preceding list of compounds of the type R·CO·R′ shows that the methoxy-group, and particularly the dimethylamino-group, increases the reactivity of the carbonyl group.

…r influence is greatest in the ortho-, and least in the meta-, position. …e it is well-known that auxochromes intensify colour, the …llelism between colour and unsaturation is manifested once again. …introduction of an acyl group into the hydroxyl or amino-group …ch weakens the colour of the substance) causes a diminution in …reactivity of the carbonyl group.

…veral other points, such as Kauffmann's inversion of chromo…res and an explanation of the action of auxochromic groups, are …cussed in the light of the theory that the reactivity of a group is …endent on its degree of unsaturation.

The following new compounds are described. The great majority of …m have been obtained by the decomposition at 130—153° of the …tive compound of diphenylketen and a carbonyl compound. *…thoxytriphenylethylene*, $OMe\cdot C_6H_4\cdot CH{:}CPh_2$, m. p. 81—82°, white …ls; *p-dimethylaminotriphenylethylene*, $NMe_2\cdot C_6H_4\cdot CH{:}CPh_2$, … 126—127°, autoxidisable, yellow or yellowish-green crystals; *…enyl-p-tolylethylene*, $CPh_2{:}CPh\cdot C_6H_4Me$, m. p. 153°; *diphenyldi-…thylene*, $CPh_2{:}C(C_6H_4\cdot OMe)_2$, m. p. 159—160°, colourless …; *p-dimethylaminotetraphenylethylene*, $NMe_2\cdot C_6H_4\cdot CPh{:}CPh_2$, … 173°; *tetramethyl-pp'-diaminotetraphenylethylene*,

$$CPh_2{:}C(C_6H_4\cdot NMe_2)_2,$$

… 211—212°, yellowish green crystals; *ae-tetramethyl-pp'-diamino-…yl-γ-diphenylmethylene-Δ^{ad}-pentadiene*,

$$CPh_2{:}C(CH{:}CH\cdot C_6H_4\cdot NMe_2)_2,$$

… 169—170°, yellowish-brown crystals; *benzhydrylidenebenzo*cyclo-*…tadiene*, $C_6H_4<\begin{smallmatrix}CH{:}CH\\CH{:}CH\end{smallmatrix}>C{:}CPh_2$, m. p. 92°, yellow crystals; *…hydrylidenedimethylbenzo*cyclo*heptadiene*,

$$C_6H_4<\begin{smallmatrix}CH{:}CMe\\CH{:}CMe\end{smallmatrix}>C{:}CPh_2,$$

… 128·5—129°, colourless crystals; *benzhydrylidenediphenylbenzo-…heptadiene*, m. p. 181—182°.

Dimethylaminoacetophenone, m. p. 105·5°, is obtained in small yield …ating dimethylaniline, acetic anhydride, and zinc chloride for four …s (the substance, m. p. 58°, described as *p*-dimethylaminoaceto…none in the literature is the monomethylated compound). *γ-Benz…hydrylidenepentamethylene oxide*, $O<\begin{smallmatrix}CH{:}CH\\CH{:}CH\end{smallmatrix}>C{:}CPh_2$, m. p. 86°, …ke pyrone itself, possesses very weak basic properties. *Dimethyl-…methylenecamphor*, $C_8H_{14}<\begin{smallmatrix}C{:}CH\cdot NMe_2\\ | \\ CO\end{smallmatrix}$, m. p. 63—64°, is pre-…d by treating a well-cooled, methyl-alcoholic solution of oxy-…ylenecamphor with the calculated amount of alcoholic dimethyl-…ne.

C. S.

…tereoisomeric Chloroimino-ketones. Peter P. Peterson (…er. Chem. J., 1911, **46**, 325—344).—In a preliminary paper, …tz and Peterson (Abstr., 1910, i, 323) have described the *a*- and …oimides of *p*-chlorobenzophenone. A full account of the work … given, together with a description of the *a*- and *β*-chloroimides …methoxybenzophenone and *pp*-chloromethoxybenzophenone.

Chloroiminobenzophenone, $CPh_2:NCl$, m. p. 37°, prepared by the action of hypochlorous acid on iminobenzophenone, forms ... crystals.

a-Chloroimino-p-methoxybenzophenone, $OMe\cdot C_6H_4\cdot CPh:NCl$, ... crystallises in thin plates; the *β-compound*, m. p. 54°, forms ... asymmetric crystals. The two forms were proved to be structurally identical by treating them with dry hydrogen chloride, thus converting them both into chloroimino-*p*-methoxybenzophenone hydrochloride, which is decomposed by water into ammonium chloride and *p*-methoxybenzophenone.

p-*Chloro-p-methoxybenzophenone*, $C_6H_4Cl\cdot CO\cdot C_6H_4\cdot OMe$, ... was prepared by the action of anisole on *p*-chlorobenzoyl chloride in presence of aluminium chloride. *a-Chloroimino-p-chloro-p-methoxybenzophenone*, $ClC_6H_4\cdot C(:NCl)\cdot C_6H_4\cdot OMe$, m. p. 94°, forms thin plates; the *β*-compound, m. p. 65°, large crystals; their structural identity ... proved in the same way as in the previous case.

o-*Chloro-p-methoxybenzophenone*, $C_6H_4Cl\cdot CO\cdot C_6H_4\cdot OMe$, ... from *o*-chlorobenzoyl chloride and anisole, has b. p. 250°/50 mm.

E. G.

δ-Phenylbutyl Ketones and δ-Phenylvaleric Acid. WALTER BORSCHE (*Ber.*, 1911, **44**, 2594—2596).—The unsaturated condensation products of cinnamaldehyde and ketones obtained by the author (Abstr., 1910, i, 680) have been reduced by Paal's method with hydrogen and colloidal palladium to the corresponding saturated substances, thus yielding a series of ketones containing the group $CH_2Ph\cdot[CH_2]_3\cdot CO\cdot$, and therefore designated δ-phenylbutyl ketones. The simplest member, *δ-phenylbutyl methyl ketone*, $CH_2Ph\cdot[CH_2]_3\cdot ...$, prepared from cinnamylideneacetone in cold methyl alcohol, is a highly refractive liquid, b. p. 268—269°, with a characteristic sweet odour; its *oxime* has b. p. 179—180°/12 mm. When shaken with a solution of bromine in 5% sodium hydroxide at 0°, the ketone yields bromoform, *δ-phenylvaleric acid*, m. p. 61°, in 35% yield, and the methyl ester, b. p. 173°/35 mm., of the acid.

β-Keto-αα-dialkyl Alcohols. III. EDMOND E. BLAISE and HERMAN (*Ann. Chim. Phys.*, 1911, [viii], 23, 522—544. Compare Abstr., 1910, i, 534).—A continuation of the work described ... (*loc. cit.*), the investigation being now extended to ketones containing a phenyl group.

*Phenyl acetoxy*tert.-*butyl ketone*, $OAc\cdot CH_2\cdot CMe_2\cdot COPh$, ... 155·5—156·5°/11 mm., prepared by the general method (Abstr., ... i, 248), furnishes a p-*nitrophenylhydrazone*, m. p. 125°, crystallising in long, orange-yellow needles from alcohol, and on hydrolysis by a 10% solution of potassium hydroxide in water yields *phenyl hydroxy*tert.-*butyl ketone*, b. p. 152—153°/12 mm. The latter furnishes an *oxime*, m. p. 122·5°, crystallising in slender needles, a p-*nitrophenylhydrazone*, m. p. 157°, forming yellow needles, and a *phenylurethane*, m. p. 89°, crystallising in long needles from benzene on adding light petroleum. Both phenyl hydroxy*tert.*-butyl ketone and its ... derivative give on hydrolysis by warm alkalis phenyl isopropyl ketone

formaldehyde. On dehydration by phosphoric oxide, phenyl ...tert.-butyl ketone might be expected to yield tiglylbenzene or ...ethylacrylbenzene, but the substance actually produced in this ...tion appears to be *benzoylmethylcyclopropane*, $COPh\cdot CMe<\begin{matrix}CH_2\\ CH_2\end{matrix}$, ... 117—119°. This gives a p-*nitrophenylhydrazone*, m. p. 175°, as ...stalline, yellow powder. *Tiglylbenzene* [*phenyl α-methylpropenyl* ...], $COPh\cdot CMe{:}CHMe$, b. p. 117·5°/10 mm., obtained by con...ing tiglyl chloride with zinc phenyl bromide, yields a p-*nitro*...*hydrazone*, m. p. 136°, crystallising in long, yellowish-red ... *Dimethylacrylbenzene* [*phenyl* iso*butenyl ketone*],

$$COPh\cdot CH{:}CHMe_2,$$

... 117°/10 mm., similarly prepared, gives a p-*nitrophenylhydrazone*, m. p. 132°, which crystallises from warm alcohol.

...*Acetoxy-β-phenylpivalyl chloride*, $OAc\cdot CHPh\cdot CMe_2\cdot COCl$, b. p. ... mm., m. p. 41°, is readily converted into the corresponding ...*amide*, m. p. 191—192°. With zinc ethyl iodide, it condenses to ...*ethyl β-acetoxy-β-phenyl*tert.-*butyl ketone*, $OAc\cdot CHPh\cdot CMe_2\cdot COEt$, ... 160—165°/11 mm., m. p. 42°, with some acetoxyphenylpivalyl ...hydride and *iso*butenylbenzene (nitrosite, m. p. 154°). From the ... of these products the corresponding keto-alcohol could not be ...ated, since in contact with alkalis the acetoxy-compound readily ...mposed into benzaldehyde and ethyl *iso*propyl ketone. As the ...alcohol could not be isolated, its dehydration could not be studied. ...should furnish *dimethylatropylethane*, $CMe_2{:}CPh\cdot COEt$, b. p. 124°/... mm., which was prepared by condensing *dimethylatropyl chloride*, ... p. 120·5°/11 mm. (p-*toluidide*, m. p. 135—136°, slender needles), ... zinc ethyl iodide. It furnishes a p-*nitrophenylhydrazone*, m. p. ..., crystallising in yellowish-red needles from alcohol. T. A. H.

The Nature of the Carbon Double Linking. III. The ...mides of Anisylidenecinnamylideneacetone. HUGO BAUER ... HEDWIG DIETERLE (*Ber.*, 1911, **44**, 2691—2697).—Anisylidene...namylideneacetone (*p*-methoxystyryl β-styrylvinyl ketone),

$$CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CH{:}CH\cdot C_6H_4\cdot OMe,$$

... be prepared by condensing *p*-methoxystyryl methyl ketone with ...namaldehyde by means of potassium hydroxide in alcoholic solution ...(compare Scholtz and Einhorn, Abstr., 1896, i, 368). When treated ... bromine in glacial acetic acid solution, it yields a *dibromide*,

$$CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CHBr\cdot CHBr\cdot C_6H_4\cdot OMe,$$

... a *tetrabromide*,

$$CHPh{:}CH\cdot CHBr\cdot CHBr\cdot CO\cdot CHBr\cdot CHBr\cdot C_6H_4\cdot OMe,$$

...crystallising in small, colourless needles, m. p. 139—140° and ... 156° respectively. The bromine atom adjacent to the anisyl ...group in these compounds is very mobile, and is readily replaced by ...alkyloxy groups.

...*Bromo-η-methoxy-α-phenyl-η-*p-*anisyl-Δ^{αγ}-heptadien-ε-one*,

$$CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe,$$

...pared by boiling the dibromide with methyl alcohol, crystallises in ... yellow plates, and gives a deep bluish-violet coloration with ...strong sulphuric acid; the corresponding *ethoxy*-compound is an oil.

ζ-Bromo-η-acetoxy-α-phenyl-η-p-anisyl-Δ$^{\alpha\gamma}$-heptadien-ε-one,

CHPh:CH·CH:CH·CO·CHBr·CH(OAc)·C_6H_4·OMe,

obtained by the action of magnesium acetate on the dibromide in [illegible] alcoholic solution, crystallises in stout, pale yellow prisms, m. p. [illegible].

γδζ-Tribromo-η-methoxy-α-phenyl-η-p-anisyl-Δ$^{\alpha}$-hepten-ε-one,

CHPh:CH·$[CHBr]_2$·CO·CHBr·CH(OMe)·C_6H_4·OMe,

prepared either by boiling *p*-methoxystyryl β-styrylvinyl [illegible] tetrabromide with methyl alcohol or by the addition of bromine [illegible] the preceding bromomethoxy-compound in glacial acetic acid [illegible] crystallises in slender, white needles, m. p. 176—177·5°. When [illegible] with pyridine, it loses hydrogen bromide, yielding *γζ-dibromo-η-methoxy-α-phenyl-η-p-anisyl-Δ$^{\alpha\gamma}$-heptadien-ε-one*,

CHPh:CH·CBr:CH·CO·CHBr·CH(OMe)·C_6H_4·OMe,

which forms yellowish-brown leaflets, m. p. 174—175°.

That the addition of bromine to *p*-methoxystyryl β-styrylvinyl [illegible] takes place at the double linking adjacent to the anisyl group [illegible] proved by the oxidation of the above-mentioned ζ-bromo-η-methoxy-[illegible] phenylanisylheptadienone by means of potassium permanganate [illegible] acetone solution to anisaldehyde and αβ-dihydroxy-γ-phenyl-[illegible] lactone (Fischer and Stewart, Abstr., 1892, 1447). F. B.

Acylated Phenanthrenes and Some of their Derivatives. CONRAD WILLGERODT and BRUNO ALBERT (*J. pr. Chem.*, 1911, [illegible], 383—394).—*9-Acetylphenanthrene*, $C_{16}H_{12}O$, prepared by the [illegible] action of acetyl chloride and phenanthrene in carbon [illegible] solution in the presence of aluminium chloride, crystallises in leaflets, m. p. 123°, having a bluish fluorescence; it yields an *oxime*, crystallising in leaflets, m. p. 80°, and a *phenylhydrazone*, light yellow [illegible], m. p. 181°. When oxidised with five to six times its weight [illegible] chromium trioxide in glacial acetic acid solution, the ketone [illegible] the ordinary form of phenanthraquinone, crystallising in [illegible] m. p. 205°. Oxidation with twice its weight of chromium [illegible] results in the formation of a second modification, which crystallises [illegible] lustrous, golden leaflets, m. p. 204—205°, and is converted by dissolving in cold concentrated sulphuric acid or by prolonged heating [illegible] alcoholic potassium hydroxide into the ordinary form; the same [illegible] formation takes place when the leaflets are heated at [illegible]. Both forms yield with *o*-phenylenediamine the same phenanthraphenazine, m. p. 219—220°. When heated with yellow ammonium sulphide at 170—180°, acetylphenanthrene yields *9-phenanthr[illegible]acetamide*, $C_{16}H_{13}ON$, crystallising in white leaflets, m. p. [illegible], together with *9-phenanthrylacetic acid*, $C_{14}H_9$·CH_2·CO_2H, which crystallises in small needles, m. p. 213—215°, and forms a yellow, gelatinous *silver* salt.

9-αα-Dichloroethylphenanthrene, $C_{14}H_9$·$CMeCl_2$, prepared from 9-acetylphenanthrene and phosphorus pentachloride, crystallises in small, yellow needles, which decompose at 80—100° without melting.

Acetylphenanthrene is reduced by zinc and glacial acetic acid to 9-phenanthrylmethylcarbinol (Pschorr, Abstr., 1906, i, 820), and by hydriodic acid and phosphorus to *9-ethylphenanthrene*, $C_{16}H_{14}$, which forms lustrous needles, m. p. 61°.

The interaction of phenanthrene and excess of acetyl chloride in the [presence] of aluminium chloride yields 9 : 10-*diacetylphenanthrene*, $C_{14}H_8(COMe)_2$, which crystallises in white needles, m. p. 178°, having a [blue] fluorescence, and forms a *phenylhydrazone*, m. p. 189°, a *bisphenylhydrazone*, $C_{14}H_8(CMe\!:\!N\cdot NHPh)_2$, small, yellow needles, m. p. 238°, and [a] *dioxime*, leaflets, m. p. 258—260°. When oxidised with chromium [tr]ioxide in glacial acetic acid solution, the diacetyl derivative is [con]verted into *phenanthrene*-9 : 10-*diketodicarboxylic anhydride*,

$$\begin{matrix}C_6H_4\cdot C\cdot CO\cdot CO \\ \quad\;\; \| \\ C_6H_4\cdot C\cdot CO\cdot CO\end{matrix}\!\!>\!O\,;$$

[wh]ich forms a light yellow powder, m. p. above 360°, and yields a yellow [sil]ver salt, $C_{14}H_8(CO\cdot CO_2Ag)_2$.

By methods similar to those described in the case of the monoacetyl [de]rivative, 9 : 10-diacetylphenanthrene has been converted into 9 : 10-[di]-*a-hydroxyethylphenanthrene*, $C_{14}H_8(CHMe\cdot OH)_2$, crystallising in [lea]flets, m. p. 165—166°, 9 : 10-*di-aa-dichloroethylphenanthrene*,

$$C_{14}H_8(CMeCl_2)_2,$$

[w]hich forms yellow leaflets, decomposing at 130—140° without melting, and 9 : 10-*diethylphenanthrene*, which crystallises in large, lustrous [lea]flets, m. p. 90—91°.

[9-]*Benzoylphenanthrene*, $C_{14}H_9\cdot COPh$, forms lustrous, white needles, [m.] p. 127°, and yields 9-*benzylphenanthrene*, crystallising in large, white [lea]flets, m. p. 91—92°, when distilled with zinc dust in a stream of [h]ydrogen.

9 : 10-*Dibenzoylphenanthrene* forms leaflets, m. p. 317°; it is reduced [b]y phosphorus and hydriodic acid at 180—190° to 9 : 10-*dibenzylphenanthrene*, which crystallises in needles, m. p. 180—182°. F. B.

The Two Forms of *o*-Benzoquinone. FRIEDRICH KEHRMANN (*Ber.*, 1911, **44**, 2632—2633).—The author is of opinion that the [q]uestion, whether the two modifications of *o*-benzoquinone are isomeric [a]nd desmotropic, has not been answered; especially, a certain proof [h]as not been given that the colourless form has the peroxide formula [a]nd the coloured form the diketo-formula. The colourless form has [no]t been analysed, and might well be a hydrated *o*-benzoquinone, $O\!:\!C_6H_4\!:\!(OH)_2$, or even an additive compound containing ether [(c]ompare Willstätter and Müller, this vol., i, 728). C. S.

Action of Magnesium Methyl Iodide on *p*-Xyloquinone and Toluquinone. EUGEN BAMBERGER and LOUIS BLANGEY (*Annalen*, 1911, **384**, 272—322).—The action of magnesium methyl iodide [o]n *p*-xyloquinone has been examined very thoroughly, and on [t]oluquinone more superficially. In the former reaction the product [o]btained after the usual operations consists of unchanged material, [a]morphous substances, about 25% of *p*-xyloquinol, ψ-cumoquinol [(]1 : 2 : 5-trimethylquinol), ψ-cumenol, 2 : 2 : 5-*trimethyl*-2 : 3-*dihydro*-p-*benzoquinone*, $CO\!<\!\begin{matrix}CMe_2\cdot CH_2\\ CH{=}CMe\end{matrix}\!>\!CO$, and smaller amounts of prehnitol, [te]tramethylcyclo*hexandione*, and *di*-p-*xyloquinol monomethyl ether*, [t]ogether with resinous and oily substances.

2 : 2 : 5-*Trimethyl*-2 : 3-*dihydro*-p-*benzoquinone*, [1 : 1 : 4-*trimethyl*-

Δ^{3}-cyclo*hexene-2 : 5-dione*] m. p. 86°, crystallises in large, highly refractive, yellow prisms, has an odour of camphor, is extremely volatile with steam, and forms a p-*nitrophenylhydrazone*, $C_{15}H_{17}O_{3}N_{3}$ (two forms, one having m. p. 244·5—245·5°, the other decomposing at 306—308°), and a *bis-semicarbazone*, $C_{11}H_{18}O_{2}N_{6}$, blackening at 400°. *Tetramethyl*cyclo*hexanedione*, which may have the constitution $CO<\begin{matrix}CH_2\cdot CMe_2\\ CMe_2\cdot CH_2\end{matrix}>CO$ or

$$CO<\begin{matrix}CHMe\cdot CHMe\\ CHMe\cdot CHMe\end{matrix}>CO$$

(the former being the more probable), forms colourless prisms, m. p. 110—111°, has an odour of borneol and peppermint, is extremely volatile with steam, and forms a *bis-semicarbazone*, $C_{12}H_{22}O_{2}N_{6}$, m. p. 330° (decomp.). *Di-p-xyloquinol monomethyl ether*,

$$CO<\begin{matrix}CH:CMe\\ CMe:CH\end{matrix}>C(OMe)\cdot C(OH)<\begin{matrix}CMe:CH\\ CH:CMe\end{matrix}>CO,$$

m. p. 220—220·5°, colourless needles, forms an *acetyl derivative*, $C_{19}H_{22}O_{5}$, m. p. 191—192°, p-*nitrophenylhydrazone*, $C_{23}H_{25}O_{5}N_{3}$, m. p. 272—272·5°, and a *semicarbazone*, $C_{18}H_{23}O_{4}N_{3}$, m. p. 272—273°.

3 : 4-Xyloquinol, toluhydroquinone, *p*-xylohydroquinone, and *p*-toluquinol have been isolated from the product obtained from toluquinone and magnesium methyl iodide.

An examination of the constitutions of the preceding substances shows that in *p*-xyloquinone and toluquinone, which contain the system $\overset{1}{O}:\overset{2}{C}\cdot\overset{3}{C}:\overset{4}{C}\cdot\overset{5}{C}:\overset{6}{O}$, the addition of the magnesium methyl iodide occurs in the 1 : 2- or the 1 : 4-, but not in the 1 : 6-, position (compare Kohler, Abstr., 1905, i, 358). Consequently, the authors believe that during the reduction of quinones to hydroquinones the addition of the hydrogen does not take place directly at the oxygen atoms of the quinone, but in the 1 : 2- and 1 : 4-positions (above scheme), the hydroquinone being produced subsequently by intramolecular change.

C. S.

[Preparation of Anthraquinone Derivatives.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234518).—When halogenated aromatic sulphones are boiled with α-aminoanthraquinones in a suitable solvent (such as nitrobenzene or naphthalene) in the presence of a condensing agent (copper acetate), compounds having valuable tinctorial properties are formed.

The *product* from α-aminoanthraquinone (1 mol.) and *pp*-dibromosulphobenzide forms brownish-red crystals, whilst the employment of 4-amino-1-benzylaminoanthraquinone and the foregoing sulphone furnishes a *compound*, violet crystals, which in the vat dyes wool a very fast violet colour.

The tinctorial properties of these and other compounds of a similar nature are tabulated in the original.

F. M. G. M.

Preparation of Aminoanthraquinones and of Aminonaphthanthraquinones or their Derivatives. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234917).—Aminoanthraquinones and aminonaphthanthraquinones may be prepared by heating halogenated

...ylbenzoic acids with ammonium hydroxide under pressure in the ...ence of a catalyst (such as copper), and submitting the amino-...ds so obtained to the action of a dehydrating agent.

4(5)-Chloro-2-p-*toluoylbenzoic acid*, m. p. 168—170° (prepared from ...uene and 4-chlorophthalic anhydride), was heated at 190—195° ...ring twelve hours with 20% ammonium hydroxide in the presence ...copper powder, the solution just acidified, and then neutralised ...th sodium acetate, when the *amino-acid* separated as a greyish-...low powder.

2-Amino-6(7)-*methylanthraquinone*, orange-yellow needles, m. p. ...6—257°, was obtained by heating the foregoing amino-acid at 200° ...h 10 parts of 90% sulphuric acid and subsequent crystallisation ...m xylene.

3(6)-Chloro-2-p-*toluoylbenzoic acid* (prepared from toluene and ...hlorophthalic anhydride) yielded an *amino-acid* (pale grey powder), ...ch was subsequently converted into 1-*amino*-6(7)-*methylanthra-...none*, red needles, m. p. 175°.

...Chloro-2-m-*xyloylbenzoic acid*, m. p. 162°, obtained from phthalic ...ydride and *o*-chloro-*m*-xylene, gave an *amino-acid* crystallising in ...e yellow needles, m. p. 140° (decomp.), and subsequently furnished ...ino-2 : 4-*dimethylanthraquinone*, dark red crystals, m. p. 293°.

...5)-Chloro-2-*naphthoylbenzoic acid*, m. p. 175° (prepared from ...hthalene and 4-chlorophthalic anhydride), yielded a grey ...ino-acid, which was converted into an *aminonaphthanthraquinone*, ...tening, red needles, m. p. 238°.

Chloro-2-naphthoylbenzoic acid, m. p. 217—220°, obtained from ...halic anhydride and 2-chloronaphthalene, gave an *amino-acid* ...dark yellow powder), and finally an *aminonaphthanthraquinone*, ...wnish-violet, glistening needles, m. p. 182°. F. M. G. M.

Preparation of Condensation Products in the Anthracene ...ies. Badische Anilin- & Soda-Fabrik (D.R.-P. 234977).—...hraquinone-1 : 5-*bisanthranilic acid*, a dark violet powder, is pre-...red by heating potassium anthranilate in nitrobenzene solution with ...5-dichloroanthraquinone in the presence of a condensing agent; ...hen this is heated at 100° with concentrated sulphuric acid, it ...rnishes a condensation product in the form of a blue powder.

Anthraquinone-1 : 5-*bis*-*o*-*thiolbenzoic acid*, an orange-red powder, ...tained in a similar manner from 1 : 5-dichloroanthraquinone and ...tassium *o*-thiolbenzoate in alcoholic solution, yields when heated at ...higher temperature with sulphuric acid (23% anhydride) a product ...hich forms a red powder. These compounds have probably the ...nstitution: $C_6H_4{<}^{X}_{CO}{>}C_6H_2{<}^{CO}_{CO}{>}C_6H_2{<}^{X}_{CO}{>}C_6H_4$, where X is ...ther sulphur or an imino-group. F. M. G. M.

Preparation of Anthraquinone Condensation Products. ...adische Anilin- & Soda-Fabrik (D.R.-P. 234922).—When 2-amino-...thraquinone is boiled (in nitrobenzene solution) with trichloro-

methyl mercaptan in the presence of a condensing reagent (such as copper), s-*dianthraquinonylthiocarbamide*,

$$CS\left(NH\cdot C_6H_3<\substack{CO\\CO}>C_6H_4\right)_2,$$

is obtained in the form of a red powder.

The tinctorial properties of this and similar compounds obtained from 1 : 4-diaminoanthraquinone, αβ-diaminoanthraquinone, β-aminoanthrarufin, 1-aminoanthraquinone, 1 : 4-aminohydroxyanthraquinone, and 1 : 5-diaminoanthraquinone respectively are tabulated in the original. F. M. G. M.

Chrysophanic Acid, Frangula-Emodin, and Some Oxonium Compounds of Anthracene Derivatives. OTTO FISCHER and HANS GROSS (*J. pr. Chem.*, 1911, [ii], 84, 369—382).—Chrysophanic acid may be obtained from chrysarobin by oxidation with chromic acid and demethylation of the resulting product by heating with hydrochloric acid in acetic acid solution. The mixture of chrysophanic acid and emodin thus obtained is separated by means of aqueous sodium carbonate. Successive treatment of the mixture with potassium hydroxide and methyl sulphate yields emodin trimethyl ether and chrysophanic acid dimethyl ether.

The transformation of diacetylchrysophanic acid into diacetylrhein is best accomplished by oxidation with chromic acid at 50—60° in a solution of equal parts of acetic anhydride and glacial acetic acid.

Dibenzoylchrysophanic acid, prepared by heating chrysophanic acid with benzoyl chloride in the presence of pyridine, crystallises in slender needles, m. p. 212° (compare de la Rue and Müller, this Journ., 1857, 10, 298). It is converted by oxidation with chromic acid into *dibenzoylrhein*, which crystallises in stellar aggregates of yellow prisms, m. p. 253—255°, and gives a red coloration with concentrated sulphuric acid.

When heated with concentrated ammonia, chrysophanic acid yields a *compound*, $C_{15}H_{11}O_3N$, crystallising in slender needles of a bronze lustre. The compound has the character of an amide, dissolves in alkalis and ammonia, forming reddish-violet solutions, and gives an orange coloration with sulphuric acid; the *ammonium* salt is unstable.

Triacetylemodin, prepared from frangula-emodin by heating with acetic anhydride and sodium acetate, has m. p. 196—197° (Liebermann gives 190°). It is oxidised by chromic acid to *triacetylemodic acid*, $C_{21}H_{14}O_{10}$, which crystallises in slender, yellow needles, and is hydrolysed by aqueous potassium hydroxide to *emodic acid*, $C_{15}H_8O_7$. The latter compound crystallises in orange-yellow needles, which decompose at 340—360°, and dissolve in alkalis with a reddish-violet coloration; it has the constitution of a trihydroxy-β-anthraquinonecarboxylic acid.

[With P. NEBER.]—A large number of anthracene derivatives have been studied with respect to their ability to form oxonium salts. Whilst anthracene and its methyl and chloro-derivatives together with anthraquinone, the methylanthraquinones, dimethyldihydroanthra-

[quinone], and diethyldihydroanthraquinone do not yield oxonium salts with perchloric and hydrobromic acids, and the hydroxyanthraquinones give at most yellowish-red or red solutions, the alkyloxy-derivatives of anthraquinone often yield stable salts. From this the conclusion is drawn that the presence both of carbonyl and alkyloxy-groups is essential for the formation of stable oxonium salts in the anthracene series.

The following salts, all of which are red in colour, were isolated: the *hydrobromide*, $C_{18}H_{17}O_5Br$, the *zincibromide*, $C_{18}H_{17}O_5Br_3Zn$, and the *perchlorate*, $C_{14}H_{17}O_9Cl$, of emodin trimethyl ether; the *hydrobromide* and *zincibromide*, $C_{17}H_{15}O_4Br_3Zn$, of chrysophanic acid dimethyl ether, and the *hydrobromide* and *zincibromide* of dimethylchrysazin (1:8-dimethoxyanthraquinone). The hydrochlorides and zincichlorides may also be isolated, but these are more unstable than the corresponding bromides. The salts of 1:2-, 1:4-, 1:5-, and 1:6-dimethoxyanthraquinone and of rufigallol hexamethyl ether with perchloric or hydrobromic acid are too unstable to be isolated.

Rufigallol hexamethyl ether, $C_{20}H_{20}O_8$, prepared by the action of methyl sulphate on its potassium salt in the presence of anhydrous potassium carbonate, crystallises in light yellow needles, m. p. 240°.

F. B.

Relationship between Chrysophanic Acid, Aloe-Emodin, and Rhein. OTTO A. OESTERLE (*Arch. Pharm.*, 1911, **249**, 445—449).

It is now shown that on reduction aloe-emodin furnishes chrysophanhydranthrone, and this on oxidation by air in presence of sodium hydroxide solution furnishes chrysophanic acid. This observation in conjunction with those recorded already (Abstr., 1903, i, 356; 1908, i, 905; 1909, i, 946, and following abstract; Léger, Abstr., 1902, i, 549; Frobenius and Hepp, Abstr., 1907, i, 428; Robinson and Simonsen, Trans., 1909, **95**, 1085; Fischer, Falco, and Gross, Abstr., 1911, i, 309, and Tutin and Clewer, Trans., 1911, **99**, 946) indicates that rhein, aloe-emodin, and chrysophanic acid are 1:8-dihydroxyanthraquinones containing respectively a $-COOH$, $-CH_2OH$, and $-CH_3$ group in position 2.

T. A. H.

Constitution of Frangula-Emodin. OTTO A. OESTERLE and W. SYPKENS-TOXOPÉUS (*Arch. Pharm.*, 1911, **249**, 311—321).—The previous formulation of emodin as 3:6:7-trihydroxy-2-methylanthraquinone (Oesterle and Tisza, Abstr., 1908, i, 350) is of doubtful validity in view of Oesterle and Johann's observation (Abstr., 1910, i, 860) that methyl sulphate methylates both hydroxyl groups of chrysophanic acid, although one is probably in the α- and the other probably in the β-position. The results of investigations of the action of ethyl chloroacetate on emodin, and of aniline on tetranitro-emodin, indicate that two hydroxyls are in the α-position and one in the β-position, whence emodin is either 1:6:8-trihydroxy-2-methylanthraquinone or 1:5:7-trihydroxy-2-methylanthraquinone.

Emodin reacts with ethyl chloroacetate to form chiefly *ethyl*

emodinglycollate diacetate, $C_{14}H_4O_4Me(OAc)_2\cdot O\cdot CH_2\cdot CO_2Et$, m. p. 192—193°, which crystallises from alcohol on addition of chloroform, and when heated with potassium hydroxide in alcohol furnishes *potassium emodinglycollate*, crystallising in red needles. A small amount of *ethyl emodindiglycollate acetate*,

$$C_{14}H_4O_2Me(O\cdot CH_2\cdot CO_2Et)_2\cdot OAc,$$

m. p. 152°, crystallising from 95% alcohol in bright yellow, slender needles, or from dry alcohol in thick needles, is formed. On hydrolysis this furnishes a *product*, m. p. 252—253° (decomp.), crystallising from pyridine on addition of alcohol.

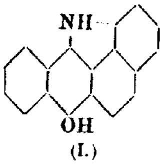
Tetranitro-emodin, obtained by nitration of emodin with nitric acid (D 1·486—1·500), crystallises from acetic acid in orange-yellow needles and explodes when heated. When boiled with aniline during two hours, it furnished bluish-violet flocks of a *substance*, which agreed in ultimate composition with that required by the formula

$$C_{15}H_8O_2(NHPh)_3(NO_2)_2(NHPh)_2,$$

that is, tetranitro-emodin in which two nitro-groups have reacted with aniline and the three hydroxyl groups have been replaced by aniline residues (D.R.-P. 89080). This substitution of hydroxyl groups by aniline residues takes place most readily when the hydroxyl groups occupy para-positions with respect to nitro-groups in hydroxy-anthraquinones (*loc. cit.*)

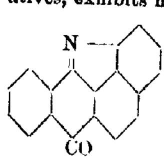
T. A. H.

Existence of Quinonoid Properties in Anthraquinone Derivatives. ROLAND SCHOLL [with G. VON WOLODKOWITSCH] (*Ber.*, 1911, **44**, 2370—2377. Compare Bally and Scholl, this vol., i, 679).—1 : 2-Benzanthraquinone when nitrated with a mixture of nitric and acetic acids and acetic anhydride yields a mixture of two yellow mono-nitro-derivatives, $C_{18}H_9O_4N$, m. p. 277—278°, and 250—251°. On reduction of the less fusible isomeride with phenylhydrazine, the corresponding amine, $C_{18}H_{11}O_2N$, is not obtained, water being eliminated between the amino- and carbonyl group, and the anhydro-compound further reduced to *O,N*-dihydro-2 : 9-indoloanthrone (formula I), $C_{18}H_{11}ON$, a green substance. When dissolved in sodium hydroxide this compound is oxidised by the air to a brown substance, 2 : 9-indoloanthrone (formula II).



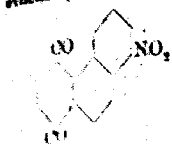
(I.)

This compound, in contrast to anthraquinone itself and its derivatives, exhibits marked quinonoid properties. It reacts energetically with phenylhydrazine, being reduced to the dihydro-compound (formula I above). It acts at the ordinary temperature in benzene or ethereal solution as an oxidising agent towards hydrogen iodide and sulphurous acid, colours hæmatoxylin red, but does not blue guaiacum resin. These pronounced quinonoid properties are considered to be due to the influence of the pyrrole nucleus attached to another nucleus of entirely different character, and so causing the existence of a carbon-nitrogen double bond of a highly unsaturated nature. This



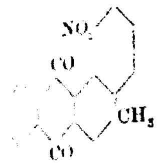
(II.)

influences the conversion of a neighbouring benzenoid linking into an ethenoid, and brings out the quinonoid properties of the anthraquinone.



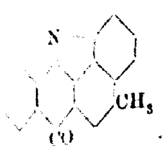
(III.)

The more fusible isomeric nitro-1 : 2-benzanthraquinone is converted on reduction into a red amino-1 : 2-benzanthraquinone, m. p. 215°, which, since it does not give a vat dye when fused with potassium hydroxide or heated with antimony pentachloride in nitrobenzene solution, is considered to have the amino-group in the benzene nucleus. The nitro-derivative accordingly has formula III.



(IV.)

3 - Methyl - 1 : 2 - benzanthraquinone when nitrated yields only one mononitro-derivative; this must have the formula IV, since it is converted on reduction into a 3-methyl-2 : 9-indoloanthrone (V), which possesses typical quinonoid properties. An isomeric 4-nitro-derivative could not be obtained, owing to the steric hindrance of the methyl group occupying the α-position in the naphthalene nucleus.



(V.)

1-*Nitro*-1 : 2-*benzanthraquinone* forms yellow plates or prisms, m. p. 277—278°. The isomeric 4-*nitro*-1 : 2-*benzanthraquinone* crystallises in slender needles, m. p. 250—251°. Both isomerides dissolve in concentrated sulphuric acid with an orange-red coloration.

4-*Amino*-1 : 2-*benzanthraquinone* forms red crystals, m. p. 215°, and dissolves in concentrated sulphuric acid with a reddish-brown coloration.

O,N-*Dihydro*-2 : 9-*indoloanthrone* is a green powder, but forms brown or brownish-red solutions with a green fluorescence.

2 : 9-*Indoloanthrone* is obtained in violet-brown flakes, which sinter at 160°, but do not melt. E. F. A.

2 : 8- or *amphi*-Chrysoquinone. ERICH BESCHKE [with FRANZ DIEHM] (*Annalen*, 1911, **384**, 173—192. Compare this vol., i, 873).—2 : 8- or amphi-*Chrysoquinone*, $C_{18}H_{10}O_2$, m. p. 288—290° (decomp.), obtained by the action of lead dioxide on a suspension of 2 : 8-dihydroxychrysene in boiling acetic acid, crystallises in reddish-yellow needles, is odourless and non-volatile with steam, reacts instantly with phenylhydrazine or acidified potassium iodide, and forms a yellow, crystalline *compound*, $C_{18}H_{10}O_2,NaHSO_3,2H_2O$, with sodium hydrogen sulphite. Its suspension in hot alcohol reacts in the presence of atmospheric oxygen with dilute sodium hydroxide to form, after acidification, 8-*hydroxy*-1 : 2-*chrysoquinone*, $OH{\cdot}C_{18}H_9O_2$, dark red needles, decomp. above 300°, and with aniline or ethylaniline to form 8-*hydroxy*-1 : 2-*chrysoquinone*-1-*anil*, $OH{\cdot}C_{18}H_9O{:}NPh$, bluish-violet crystals, m. p. 230° (decomp. at 220°). The constitutions given to the two preceding substances are based on Willstätter and Parnas' experiences of the oxidising power of quinones of different types (Abstr., 1907, i, 1056), and are supported by the following evidence.

The chief proof is the fact that aniline or ethylaniline, reacting with 2 : 8-chrysoquinone, produce the same anil. 8-Hydroxy-1 : 2-chrysoquinone, which is also easily obtained by the action of sodium hydroxide and air on a boiling alcoholic suspension of 2 : 8-diacetoxychrysene, forms a *sodium* salt, $C_{18}H_9O_3Na$, bluish-violet, almost black needles, is reduced by sodium hyposulphite to the colourless 1 : 2 : 8-*trihydroxychrysene*, and forms an *acetyl* derivative, m. p. 25[illegible], red needles, *ethyl ether*, m. p. 246°, and *benzoyl* derivative, m. p. [illegible]. It does not appreciably react at the ordinary temperature with phenylhydrazine, acidified potassium iodide, or sulphurous acid. A hot saturated solution of the quinone in glacial acetic acid reacts with concentrated alcoholic *o*-phenylenediamine to form 8-*hydroxy*-1 : 2-*chrysophenazine*, $OH\cdot C_{18}H_9<\genfrac{}{}{0pt}{}{N}{N}>C_6H_4$, m. p. 292°, yellow needles, the *benzoyl* derivative, m. p. 270°, *acetyl* derivative, m. p. 252°, and *ethyl ether*, m. p. 215°, of which are respectively identical with the substituted chrysophenazines obtained by condensing *o*-phenylenediamine with the corresponding derivatives of 8-hydroxy-1 : 2-chrysoquinone.

8-Hydroxy-1 : 2-chrysoquinone-1-anil yields 8-hydroxy-1 : 2-chrysoquinone by hydrolysis with mineral acids, and yields with acetic anhydride an *acetyl* derivative, $C_{26}H_{17}O_3N$, m. p. 215°, which is converted by dilute hydrochloric and a little acetic acid into 8-acetoxy-1 : 2-chrysoquinone.

1 : 2 : 8-*Triacetoxychrysene*, $C_{18}H_9(OAc)_3$, colourless crystals, m. p. 195°, is obtained by treating a solution of 8-acetoxy-1 : 2-chrysoquinone in boiling acetic anhydride with zinc dust. 1 : 2 : 8-*Triethoxychrysene*, $C_{18}H_9(OEt)_3$, colourless crystals, m. p. 142°, is prepared by treating an aqueous alcoholic suspension of the sodium salt of 8-hydroxychrysoquinone, with dilute sodium hydroxide and sodium hyposulphite, and subsequently with ethyl sulphate. It has been found that 2-hydroxy-α-naphthaquinoneanil is produced when β-naphthaquinone is boiled with ethylaniline in alcoholic solution. C. S.

Condensation of Menthones with Organomagnesium Compounds. Synthesis of Homologues of Menthol. MARCEL MURAT (*J. Pharm. Chim.*, 1911, [viii], 4, 294—299).—Magnesium phenyl bromide reacts with menthone to give l-3-*phenyl*-1-*methyl*-4-*isopropyl*-3-cyclo*hexanol*, $CH_2<\genfrac{}{}{0pt}{}{CHMe\cdot CH_2}{CH_2\cdot CHPr^\beta}>CPh\cdot OH$, b. p. 175°/20 mm., D^0 0·9962, n_D 1·527, $[\alpha]_D^{20}$ −16·32°. The *racemic* form prepared in the same way from thymomenthone had b. p. 170°/18 mm., D^0 0·995[illegible]. When treated with phenylcarbimide, or passed over alumina at 300°, dehydration occurs with production of the corresponding menthenes. 3-*phenyl*-1-*methyl*-4-iso*propyl*cyclo*hexene* has b. p. 268—272°/760 mm., D^0 0·9700, n_D 1·537. $[\alpha]_D$ +13·9°.

Magnesium *cyclo*hexyl bromide slowly acts on menthone, giving 3-cyclo*hexyl*-1-*methyl*-4-iso*propyl*-3-cyclo*hexanol*, monoclinic needles, m. p. 92°, together with 3-cyclo*hexyl*-1-*methyl*-4-iso*propyl*cyclo*hexene*, b. p. 265°/760 mm., D^0 0·9897, n_D 1·498, $[\alpha]_D$ +6·2°.

Thymomenthone (inactive menthone) was prepared by passing the vapour of Brunel's thymomenthol (Abstr., 1906, i, 81) over copper at

...°, it occurs as a viscid liquid, b. p. 212°, having a less pronounced odour than natural menthone. When treated with magnesium cyclohexyl bromide, it yields r-*cyclohexylthymomenthol*, b. p. 164°/15 mm. (decomp.), D^0 0·9931, n_D^{17} 1·529; the corresponding *cyclohexylthymomenthene* has b. p. 260°/756 mm.

W. O. W.

Terpenes and Ethereal Oils. CVII. Constitution and Synthesis of Pinolone and of Dihydropinolone (3-Acetyl*iso*propyl*cyclo*pentane). OTTO WALLACH (*Annalen*, 1911, 384, 193–208).—Dihydropinolone, when prepared by the reduction of pinolone by Paal's method and purified through the *semicarbazone*, $C_{11}H_{21}ON_3$, m. p. 164—165°, is a colourless liquid with an odour of amyl acetate; it has b. p. 211°, D^{21} 0·8885, and n_D^{21} 1·4466. Its recognition as 3-acetyl*iso*propyl*cyclo*pentane, $CHAc<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}$, has been accomplished by its degradation to *iso*propyl*cyclo*pentan-3-one, and by its synthesis from this substance. Its degradation is represented essentially by the scheme: dihydropinolone $\xrightarrow{NaOBr}$ $>CH\cdot CO_2H$ (b. p. 153—156°/16 mm.) $\longrightarrow$ $>CH\cdot CO\cdot NH_2$ (m. p. 164—165°; identical with Semmler's dihydrocamphoceenamide *b* [Abstr., 1906, i, 681]) $\xrightarrow[KOH]{Br\ and}$ $>CH\cdot NH_2$ $\longrightarrow$ $>CH\cdot OH$ $\xrightarrow{CrO_3}$ *iso*propyl*cyclo*pentan-3-one.

The synthesis has been accomplished as follows: The interaction of *iso*propyl*cyclo*pentan-3-one (prepared from tanacetophorone), zinc, and ethyl α-bromopropionate in benzene leads to the formation of an hydroxy-ester, which by successive boiling with acetic anhydride, hydrolysis by alcoholic potassium hydroxide, and acidification yields an acid, $CO_2H\cdot CMe\!:\!C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}$, the distillation of which in hydrogen produces a *hydrocarbon*, $C_{10}H_{18}$, b. p. 172—174°, D^{20} 0·809, n_D 1·4506. This hydrocarbon has assigned to it the constitution $CHMe\!:\!C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}$, on account of its exalted molecular refraction and its behaviour. It is practically identical with the *hydrocarbon*, $C_{10}H_{18}$, b. p. 171—174°, D^{22} 0·812, n_D 1·4515, obtained by heating *dihydropinolol*, $OH\cdot CHMe\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CHPr^{\beta}\end{matrix}$, b. p. 215—216°, D^{20} 0·8920, n_D 1·4569 (prepared by the reduction of dihydropinolone), with zinc chloride. The synthetic hydrocarbon (from the *iso*propyl*cyclo*pentanone) forms a blue *nitrosochloride*, which by successive treatment with boiling acetic acid and sodium acetate and with sulphuric acid is converted into a *ketone*, $COMe\cdot C<\begin{matrix}CH-CHPr_{\beta}\\ CH_2\cdot CH_2\end{matrix}$ (*semicarbazone*, m. p. 182—184°), isomeric with pinolone. This ketone yields dihydropinolone when reduced by Paal's method.

The series of transformations whereby pulegone dibromide is converted into pulegenic acid (Abstr., 1903, i, 567) has suggested an explanation of the course followed by pinyl tribromide during its

conversion into pinolone. This explanation leads to the conclusion that pinolone may be either

$$CMe_2{:}C<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH\cdot COMe\end{matrix} \quad\text{or}\quad CH_2{:}CMe\cdot CH<\begin{matrix}CH_2\cdot CH_2\\ CH_2\cdot CH\cdot COMe\end{matrix}$$

In harmony with this, the author finds that pinolonesemicarbazone, m. p. 158°, can be separated by repeated crystallisation into two portions, the less fusible of which has m. p. 173°. C. S.

Degradation of Nerol and its Constitution. A. BLUMANN and OTTO ZEITSCHEL (*Ber.*, 1911, **44**, 2590—2593).—When nerol or geraniol is oxidised by 1% potassium permanganate at 0° and the product is subsequently treated with dilute chromic and sulphuric acids, acetone, lævulic acid, and oxalic acid are obtained, the amount of lævulic acid being practically the same in each case. These results confirm the view that nerol and geraniol are stereoisomerides (Zeitschel, Abstr., 1906, i, 521). C. S.

Influence of Water on the Rotatory Power of Camphor Solutions. ENDRE VON KAZAY (*Pharm. Post*, 1911, **44**, 495—496).—The value of $[a]_D$ for camphor in a number of organic solvents is about $+43\cdot6°$, independent of the nature of the solvent. The addition of water to the alcoholic or acetic acid solution causes a very marked alteration in the rotation. When the proportion of water in the alcoholic solution containing about 12% of camphor is increased from 4% to 37%, the rotation diminishes from 5·3° to 7·1°. When in acetic acid solution containing about 10% of camphor, the proportion of water is gradually increased from zero to 32·3%, the rotation gradually diminishes from 8·3° to 6·0°. If the proportion of water in a solution is known, the percentage of camphor, p, can be calculated from the formula: $p=(100d)/(l[a]/B)$, where B is 0·1308 for acetic acid solutions, and 0·12822 for alcoholic solutions. G. S.

Effect of Molecular Symmetry on the Optical Activity and Relative Rotatory Power of Aromatic Position Isomerides. THOMAS P. HILDITCH (*Zeitsch. physikal. Chem.*, 1911, **77**, 482—496. Compare Trans., 1908, **93**, 1618; 1909, **95**, 1578).—A more detailed account of work already published (compare Proc., 1910, **26**, 111). The relative effects of ortho-, meta- and para-isomerides on the rotatory power is illustrated by the behaviour of compounds containing methyl, halogen, hydroxy-, methoxy-, nitro-, and amino-groups.

Sodium camphor-β-thiosulphonate, $C_{10}H_{15}O\cdot SO_2\cdot SNa$, is prepared by interaction of camphor-β-sulphonyl chloride and sodium sulphide in boiling alcohol. It occurs in soft, colourless, crystalline masses. The corresponding *acid* is an oily substance, and unstable. The silver salt forms a cream-coloured powder. The *anhydride*, $[(C_{10}H_{15}O)\cdot SO_2]_2S$, is obtained in almost theoretical yield by boiling equivalent amounts of the sulphonyl chloride and the sodium salt dissolved in carbon tetrachloride. It occurs in pale yellow needles, m. p. 144°.

Dicamphor-β-sulphonyl disulphide, $[(C_{10}H_{15}O)\cdot SO_2]S_2$, was obtained by the action of iodine, dissolved in potassium iodide solution, on

...dium camphor-β-thiosulphonate, and also by acting on the latter with sulphur monochloride in cold carbon tetrachloride. It occurs in colourless needles, m. p. 130°.

The phenyl camphor-β-sulphonates were all prepared by a modification of the Schotten-Baumann method. *Catechol dicamphor-β-sulphonate*, $C_6H_4(SO_3\cdot C_{10}H_{15}O)_2$, forms colourless or slightly red crystals, m. p. 124°; the corresponding *resorcinol* compound melts at 129—130°, and the *quinol* compound at 187° (slight decomp.).

Pyrogallol tricamphor-β-sulphonate, $C_6H_3(SO_3\cdot C_{10}H_{15}O_3)_3$, occurs in soft, colourless needles, m. p. 148° (decomp.). The corresponding *phloroglucinol* compound forms prismatic crystals, m. p. 104—106°.

G. S.

[Essential Oils.] SCHIMMEL & Co. (*Bericht*, October 1911, pp. 1—152).—*Artemisia biennis*, according to Rabak, yields 0·03% of a dark brownish-red, sweet-smelling oil, D^{25} 0·893, $[\alpha]_D$ +4·39°, n_D^{30} 1·5181, acid number 0, ester number 16, acetyl ester number 17·28, which dissolves in 4 vols. or more of 95% alcohol, and probably contains methylchavicole. According to the same author, *Artemisia serrata* yields 0·3% of a reddish-brown, bitter oil, D^{25} 0·913, α_D +6·8°, n_D^{30} 1·4602, acid number 1·6, ester number 10·0, acetyl ester number 43, which dissolves in 0·5 or more vols. 80% alcohol, and probably contains thujone.

Barosma crenulata (round buchu) leaves yield 1·7% oil, D_{15}^{20} 0·9364, α_D −15°22′, n_D^{20} 1·48005, which dissolves in 2·5 or more vols. of 70% alcohol with separation of paraffin, is brownish-yellow in colour after removal of traces of copper by acid, has mint-like odour, possibly due to menthone, and contains very little diosphenol.

Mandarin oil pressed from unripe fruits in Valencia had D^{15} 0·8665, n_D^{20} 1·47900, acid number 0·2, ester number 17·3, was incompletely soluble in 90% alcohol, and was of dark olive-green colour.

Helichrysum angustifolium oil from Dalmatia had D^{15} 0·9005, n_D^{20} 1·48209, acid number 0·9, ester number 61·1, and dissolved in 9 or more vols. of 90% alcohol. It was of olive-green colour, and resembled camomile oil in odour.

The Jalpaiguri (Indian) lemon-grass oils referred to previously (Abstr., 1910, i, 328) have now been found to be derived from *Cymbopogon pendulus*, Stapf.

Cayenne linaloe oil, like the Mexican product, contains methylheptenol.

Dalmatian laurel-leaf oil has D^{15} 0·9268, α_D −14°36′, n_D^{20} 1·46813, acid number 0·5, ester number 29·9, acetyl ester number 68·6, and is soluble in 2·5 or more vols. of 70% alcohol.

Dalmatian myrtle oil has D^{15} 0·9254, α_D +13°20′, n_D^{20} 1·46694, acid number 1·0, ester number 134·8, acetyl ester number 186·7, and is soluble in 3·2 or more vols. of 70% alcohol.

French peppermint, cultivated in Dalmatia, gave oils which after rectification had the following range of constants, D^{15} 0·9094—0·9141, α_D −11°45′ to −18°12′, n_D^{20} 1·46041—1·46783, acid number 0—1·0, total menthol 39·6—54·1%, ester menthol 2·6—3·8% and were soluble in 2·8 to 3 vols. of 70% alcohol with slight opalescence. According to

Henderson (*Chem. & Drug.*, 1911, **79**, 216), English peppermint grown on the banks of a river yielded only 0·1% oil, D 0·9046, a_D −[illegible], total menthol 59·2%, ester menthol 3·9%, whilst that grown in open fields on clay soil gave 0·409% oil, D 0·9065, a_D −27·4°, total menthol 61·35%, ester menthol 5·57%, and a third sample grown on sandy soil gave 0·19% oil, D 0·9046, a_D −28·2°, total menthol 59·4[illegible]%, ester menthol 4·74%. Italian peppermint oil from Pancalieri had D [illegible], a_D −22°56′ to −26°51′, was soluble in 2·9 vols. of 70% alcohol, and deposited solid matter on cooling (Bourdet, *Bull. Sci. pharm.*, 1911, **18**, 372).

Sage oil distilled in Dalmatia in August from dry herb had the following normal constants, D^{15} 0·9165, a_D +25°, n_D^{20} 1·45[illegible]1, acid number 1·0, ester number 9·3, whilst oil distilled from fresh herb in May had D^{15} 0·9111, a_D +20°22′, ester number 10·3, and was less soluble in alcohol than the August oil.

Origanum hirtum a-albiflorum herb grown in Dalmatia furnished origanum oil having the following range of constants, D^{15} [illegible]— 0·94000, a_D +0°6′ to 0°20′, n_D^{20} 1·49394—1·50436, soluble in from 2·8 vols. of 70% alcohol to 1·5 vols. of 80% alcohol, and containing from 51 to 60% thymol.

Dalmatian spike oil had D^{15} 0·9022—0·9033, a_D −0°10′ to [illegible], acid number 0·9, ester number 5·4—5·6, and was soluble in from 4 to 5 vols. of 60% alcohol. *Lavandula spica* herb from Spain yielded 1·9% of brownish-yellow oil, D^{15} 0·9100, a_D −2°20′, n_D^{20} 1·46[illegible], acid number 3·7, ester number 7·0, and was soluble in 2 vols. of 70% alcohol, but became opalescent with more alcohol.

According to Jeancard and Satie (*Perf. and Essent. Oil Rec.*, 1911, **2**, 79) a so-called sandalwood from Guiana yielded oil having the following range of constants, D^{15} 0·963 to 1·0122, a_D +0°30′ to −6°, saponification value 13 to 65, after acetylation 65 to 117. On distillation it gave the following fractions: below 155°/20 mm., [illegible] to 27·4%, 155—160°/20 mm., 59 to 80%, and above 160°/20 mm., [illegible] to 13·6%. The second fraction contained a new constituent, *[illegible]*, b. p. 158—159°/20 mm., D^{23} 1·0378, a_D −6°, which dissolved in 1[illegible] vols. 70% alcohol, and was colourless, viscous, and of agreeable odour; this substance is probably a tertiary alcohol.

Star anise oil contains *d*-*a*-pinene, *d*-*β*-phellandrene, dipentene, and *l*-limonene in the lower boiling fractions; as well as a fraction, 163—168°, having a turpentine-like odour, but which is free from *β*-pinene and sabinene.

Strobilanthes lupulinus flower buds yield an oil, D 0·9648, a −1[illegible], n 1·4688, acid number 1·7, ester number 257 (*Perf. and Essent. Oil Rec.*, 1911, **2**, 96), having a strong, pleasant odour recalling those of tarragon and lavender.

A "wormwood" oil from Dalmatia had D^{15} 0·9188, acid number 1·3, ester number 64·4, and dissolved in 1 vol. 80% alcohol; it differed in odour from true wormwood oil, and was probably derived from another species of Artemisia. Wisconsin "wormwood" oil had D^{22} 0·916[illegible], saponification number 150 (forty minutes), after acetylation 234·8 to 236·2, and was dark, with a mint-like odour. It contained much thujone, and on hydrolysis gave formic and salicylic acids.

Oil from *Gaultheria fragrantissima* of the Nilgiris, India, had D^{15} 1·1877, $a_D \pm 0$, n_D^{20} 1·53485, ester number 364·8, was reddish-brown in colour and resembled winter green oil in odour.

Cananga oil from German East Africa distilled from fresh flowers had D^{15} 0·9366, $a_D - 17°1'$, n_D^{20} 1·48451, acid number 1·1, ester number 136·5 and was soluble, with opalescence in 8 or more vols. of 80% alcohol.

Artemisia coerulescens herb from Turin gave 0·24% oil, D^{40} 0·9179, $a_D - 5°50'$, acid number 11·3, ester number 42·0, which was brown and of buttery consistence, and had an odour recalling that of hyssop oil. The crystalline matter deposited by the oil melted at 108°.

Cardamom roots from Indo-China yielded 0·64% citron-yellow oil, D^{15} 0·9066, $a_D - 32°57'$, n_D^{20} 1·48151, acid number 3·7, ester number 87·9, acetyl ester number 96·7, which was different from the seed oil in odour. It contained bisabolene, cineole, and paraffin.

Juniperus procera wood sawdust from German East Africa yielded 3·2% of oil, D^{15} 0·9876, n_D^{20} 1·50893, acid number 14·9, ester number 8·4, acetyl ester number 70. Fragments of the wood gave 3·2% of oil, which was semi-solid, and, after removal of solid matter, had D^{15} 1·0289, n_D^{20} 1·51011, acid number 27·06, ester number 7·93, acetyl ester number 89·6. The deposited crystals were cedar camphor.

Cinnamomum Burmanni bark from Timor and the Celebes gave 0·5% oil, D^{15} 1·0198, $a_D - 1°50'$, n_D^{20} 1·58282, which was not so pleasant in aroma as Ceylon cinnamon bark oil, but contained 77% of aldehydes and 11% phenols.

Meriandra benghalensis leaves from Erythraea gave 1·5% bright brown oil, D^{15} 0·9513, $a_D - 2°5'$, n_D^{20} 1·47490, acid number 3·7, ester number 14·8, which had an odour resembling those of rosemary and sage. It deposited *d*-camphor when cooled.

Santolina chamaecyparissus herb from Turin gave 0·47% dark brown oil, D^{15} 0·9065, n_D^{20} 1·50040, acid number 6·6, ester number 16·4, acetyl ester number 74·2, with an odour resembling that of wormwood oil.

Satureja cuneifolia oils from Dalmatia had the following range of constants, D^{15} 0·9182 to 0·9440, $a_D - 1°50'$ to $5°15'$, n_D^{20} 1·49816 to 1·50556, and contained from 28 to 59% of phenols, chiefly carvacrol, whilst the non-phenolic portion had a strong odour of cymene.

A résumé of literature published since April, 1911, on the analysis, physical properties, chemistry, etc., of essential oils and their constituents is also given. T. A. H.

[Essential Oils.] ROURE-BERTRAND FILS (*Sci. Ind. Bull.*, 1911, [iii], 2, 1—25).—[JUSTIN DUPONT and LOUIS LABAUNE.]—"Linalyl" bromide, obtained by esterifying either geraniol or linalool (Abstr., 1910, i, 184), condenses with ethyl sodiomalonate to form the *ester*, $C_{10}H_{17}\cdot CH(CO_2Et)_2$, b. p. 158—159°/5 mm., and this on hydrolysis gives the corresponding acid, $C_{10}H_{17}\cdot CH(CO_2H)_2$, which on distillation under reduced pressure furnishes the monobasic *acid*,

$$C_{10}H_{17}\cdot CH_2\cdot CO_2H,$$

b. p. 145—146°/5 mm., the *ethyl* ester of which has b. p. 127—128°/5 mm. The $\cdot C_{10}H_{17}$ group in the ester does not appear to have the geranyl configuration, since it is unaffected by sulphuric acid of 66° Bé. On reduction with sodium in alcohol, the ester yields a new *alcohol*,

$C_{10}H_{17}\cdot CH_2\cdot CH_2\cdot OH$, D^{15} 0·8956, n_D^{15} 1·4755, b. p. 119°/5 mm., which gives a crystalline *pyruvate*, b. p. 135°/6 mm., the *semicarbazone* of which crystallises from alcohol and melts at 103°. The alcohol is also converted into the corresponding alcohol by Sabatier and Senderens' method. All these substances possess weak and not very characteristic odours.

Linalyl bromide condenses similarly with ethyl sodioacetoacetate to form the *ester*, $C_{10}H_{17}\cdot CHAc\cdot CO_2Et$, b. p. 145°/6 mm., which on hydrolysis by potassium hydroxide in alcohol gives the *ketone*, $C_{10}H_{17}\cdot CH_2Ac$. The latter was not obtained pure, but it gives a *semicarbazone*, m. p. 86°, and on oxidation yields lævulic acid as chief product.

Ruta montana from Algeria furnishes an oil, D^{15} 0·8307, a_D +0°4', soluble in 2·25 vols. 70% alcohol, which contains about 90% of methyl nonyl ketone. *Ruta bracteosa* from Algeria gives an oil, D^{15} 0·8419, a_D −4°12', soluble in two vols. 70% alcohol, and containing 80% of ketones. This oil differs also from the foregoing in congealing partly at −5°, whilst the first oil is solid at +10°.

Inula viscosa oil from Algeria had D^{15} 0·9436 a_D −24°0', and consisted chiefly of cineol.

Syrian origanum oil had D^{15} 0·9309 and a_D +1°6', and was soluble in 1·2 or more vols. 80% alcohol; on standing it deposited a translucent "camphor." Syrian thyme oil, D^{15} 0·9120, a_D −0°56', contained 43% phenols, composed of thymol and carvacrol. Syrian sage oil, D^{15} 0·9843, a_D −6°8', was soluble in 1·5 or more vols. of 70% alcohol. Syrian laurel-leaf oil had D^{15} 0·9161 and a_D −14°20', and was soluble in one or more vols. of 80% alcohol. Syrian neroli oil, D^{15} 0·875, a_D +1°6', saponification number 51·5, is similar to French neroli oil in constants. Syrian petit-grain oil had D^{15} 0·8857, a_D 3°24', saponification number 77·4, and was soluble in 1·25 or more vols. of 70% alcohol. T. A. H.

Essential Oil of Bupleurum fructicosum. II. LUIGI FRANCESCONI and G. SANNA (*Gazzetta*, 1911, 41, i, 796—813. Compare this vol., i, 658).—By fractional distillation of the essential oil of *Bupleurum fructicosum*, a large amount of a *terpene* is obtained as a mobile, colourless liquid, b. p. 167—169°, D^{14} 0·8416, a^{17} +35·7°, n_D 1·4862, which polymerises at 200°. The *polymeride* is a white, amorphous substance, m. p. 90—100° (becoming yellow), a^{14} −66·14° (in chloroform solution). The action of bromine on the terpene yields a colourless, viscous, non-crystalline substance, the amount of bromine absorbed indicating that the substance contains two double linkings. Hydrogen chloride also gives a non-crystalline product. With nitrosyl chloride, a small quantity of a *substance* was obtained, crystallising in small prisms, which begin to melt at 97°, and are entirely decomposed at 102°. When the residue from this reaction is distilled in steam, an *oil* is obtained, b. p. about 200° (partial resinification), which is dextrorotatory in alcoholic solution. The action of hydrazine and of phenylhydrazine does not yield crystalline compounds, but semicarbazide gives a *semicarbazone*, which forms silvery scales, m. p. 197—198°, and is dextrorotatory.

The essential oil also contains an *alcohol* and an *ether*. R. V. S.

Extraction of an Aldehydic Perfume from Pine-wood Tar. FRIEDRICH MÜLLER (D.R.-P. 234794).—The fractional distillation of pine-wood tar furnishes at 150—200° substances of aldehydic nature and powerful odours, an *aldehyde* thus obtained formed a light brown oily liquid of high refractive index and characteristic odour; the crude distillate (b. p. 168—185°) after refractionation had b. p. 170—175° under atmospheric pressure, 75—85°/23 mm. and 51—56°/7 mm. with D^{17} 1·117. The *semicarbazone*, m. p. 184—186°, rhombic crystals; and an *oxime*, b. p. 170° (about) and D 0·8388 were also prepared. F. M. G. M.

Analysis of a Resin from an Egyptian Sarcophagus. REUTTER (*Compt. rend.*, 1911, **153**, 597—599).—The resin from a sarcophagus of the thirtieth dynasty has been shown to contain gum styrax from *Liquidambar orientalis*, Aleppo resin from *Pinus halepensis*, mastic from *Pistacia lenticus*, cedar wood oil, and asphalt. The ash contained sodium, calcium, aluminium, magnesium, traces of arsenic, chromium, iron, and manganese, carbonates, silicates, phosphates, chlorides, sulphates, and nitrates. The resin also contained sand, vegetable particles, and mineral fragments, of which an account is given. W. O. W.

Constituents of Guayule, Parthenium argentatum. P. ALEXANDER (*Ber.*, 1911, **4**, 2320—2328).—This investigation was undertaken to ascertain, if possible, whether this plant, which is the source of guayule caoutchouc, contains any substance which can be regarded as the raw material from which caoutchouc is formed in plants. The results were negative from this point of view.

Guayule contains about 8—10% of caoutchouc, expressed on the dry material. The commercial caoutchouc from this source contains 75% of caoutchouc hydrocarbons, and does not differ from "hard Para rubber" to any greater extent than other second class rubbers. The dry plant yields about 6·5% of dark green, extractive matter to acetone, and of this 54%, 31%, and 15% are successively dissolved by light petroleum, ether, and hot alcohol, and of the three component parts thus separated, 12·1%, 7·0%, and 2·0% respectively consist of "unsaponifiable matter." The acids produced on hydrolysis of the extract include one melting at 119° and belonging to the cinnamic acid group, and phenylacetic acid. Weil states (Priv. com.) that he has found cinnamic acid in the products of hydrolysis of resin from guayule. The crude acetone extract on distillation with steam gives a *sesquiterpene alcohol*, m. p. 127—128°, with a camphoraceous odour.

On distillation with steam, guayule yields from 0·5 to 4% of volatile oil, D_{15}^{15} 0·8861, which is lævorotatory, possesses a peculiar pepper-like aroma, and consists almost wholly of hydrocarbons. On fractional distillation it gives 30%, b. p. 50—60°/17 mm.; 20·3%, b. p. 60—80°/17 mm.; 24·8%, b. p. 120—160°/17 mm., with 5% of resinous residue. The first fraction is mainly *l*-pinene, and the third fraction a *sesquiterpene*, D_{15}^{15} 0·9349, $[\alpha]_D^{16}$ − 21°24′, n_D^{16} 1·496. No styrene is present. The above relates to oil distilled from guayule in a fairly fresh state. Oil distilled from plants which had been stored several

years contained much oxygenated material, and although pinene was obtained from this oil no sesquiterpene fraction could be isolated. The presence of volatile oil in guayule is the cause of the difficulty at first experienced in the industrial use of caoutchouc from this source, since the oil hinders vulcanisation. T. A. H.

Cerebrosides of the Brain. HERMANN LOENING and HANS THIERFELDER (*Zeitsch. physiol. Chem.*, 1911, **74**, 282—289).—Methods are described for obtaining pure the galactoside known as cerebron (Thudichum's phrenosin). The presence of other galactosides of the nature of Thudichum's kerasin was also found. The work is to be carried further. W. D. H.

Saponins. RUDOLF KOBERT (*Chem. Zentr.*, 1911, **1**, 1589; from *Unna Festschrift*, 1911, **1**, 161—183).—Tables are given in the original of the chief members of the saponin series, $C_nH_{2n-8}O_{10}$, as well as of those of the digitonin series, $C_nH_{2n-18}O_{28}$, of the primary sapogenins (secondary glucosides), $C_nH_{2n-6}O_7$, and endsapogenins, $C_nH_{2n-8}O_4$, and also of sapogenins, $C_nH_{2n-6}O_3$. E. F. A.

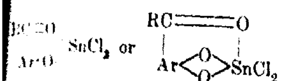
Artemisinphenylhydrazone. PASQUALE BERTOLO (*Gazzetta*, 1911, **41**, i, 705—708. Compare Abstr., 1901, i, 718; 1908, i, 560).—*Artemisinphenylhydrazone*, $C_{15}H_{18}O_3$:N·NHPh, crystallises in yellowish-white, feathery needles, m. p. 144—145° (rapid heating), 221—222° (slow heating); $[\alpha]_D^{24}$ +180° (in alcohol). After the substance has been kept at 160° for a few minutes, the rotatory power is unchanged. The compound dissolves in concentrated sulphuric acid, giving a green coloration, which becomes cherry-red on addition of a trace of nitric acid. The phenylhydrazone differs from artemisin in that it is not acted on by alkalis. Prolonged reduction with sodium amalgam yields an acid *substance*. R. V. S.

The Chlorophyll Group. The Duality of the Chlorophyllans and *allo*Chlorophyllan. LEON MARCHLEWSKI and J. MARSZALEK [with Z. LEYKO] (*Biochem. Zeitsch.*, 1911, **35**, 413—433).—Crude chlorophyll solutions from different sources, and even from the same plants, react in different ways when treated with zinc hydroxide and carbon dioxide. The chlorophyll from stinging nettles gives after treatment with these reagents for one day a fairly rapid change, but only a slight precipitate which has not the character of a zinc salt. In the chlorophyll, on the other hand, from maple leaves (*Acer pseudoplantanus*), only a small amount of the material enters into reaction with the zinc salt, and by such treatment the part which does not enter into combination can be separated from the other part. The "zinc chlorophyll" prepared from nettles contains more methoxyl and phytol when zinc acetate is employed for its preparation than when zinc hydroxide is used, and the latter exerts a slight hydrolytic action. The spectral measurements and extinction coefficients of this zinc derivative are given in some detail. Chlorophyllans were prepared from leaves of *Acer platanoides* from Poland and *A. pseudoplantanus* from Galicia and analyses are given of the products obtained and also spectroscopic measurements. The analyses do not differ markedly from one another

...e spectroscopic measurements of the preparation from *A. platinoides* ...intermediate between those obtained from nettles and maple. It ...concluded that there is here a mixture of two chlorophyllans ...lorophyllan and *allo*chlorophyllan), and that certain varieties of ...nts are rich in the latter substance. By the separation of chloro...yllan by means of zinc hydroxide and carbon dioxide from *allo*...lorophyllan (the method for which is given in detail) in a prepara...ion rich in the latter and obtained from *A. platinoides*, a specimen ...*allo*chlorophyllan was obtained of which the properties and spectro...pic measurements are given in some detail; this on saponification ...ields *allo*chlorophyllanic acids. These are reddish (and not olive-green) ...ubstances, from which fractions can be obtained by treating the ...ethereal solution with hydrochloric acid in various strengths. Only ...when 5% acid is used is any appreciable quantity of the pigment ...dissolved, and the basic character is therefore weak. By 7% acid a ...eparation of crystalline form was obtained.

S. B. S.

Lakes. I. PAUL PFEIFFER [with Z. GOLDBERG and J. KUNTNER] (*Ber.*, 1911, **44**, 2653—2662).—The author hopes to bring Tschugaeff's (Abstr., 1907, i, 17, 392, 830) and Werner's (Abstr., 1908, i, 441) ...theories of the constitution of lakes into line with the theory by which ...he explains the phenomena of halochromy (Abstr., 1910, i, 852; this ...vol., i, 788). With this object in view, he has prepared, by heating ...the following o-hydroxy-ketones with tin tetrachloride (1·5 to 2 mols.) ...in dry benzene on the water-bath, coloured substances, which are



represented by the annexed constitution. These substances are closely allied to the lakes of the tin series, which are obtained by replacing the chlorine atoms by ...hydroxyl groups. The important question whether the tin is united ...co-ordinatively with the carbonyl oxygen atom is answered in the ...affirmative, not only because the author has already shown (*loc. cit.*) ...that carbonyl compounds of the most diverse character exhibit quite ...universally a tendency to unite co-ordinatively with tin tetrahalides, ...but also for the following reason. *m*- and *p*-Hydroxyacetophenone ...and tin tetrachloride in benzene, cold or hot, form normal additive ...compounds, $Cl_4Sn<\begin{smallmatrix}O{:}CMe{\cdot}C_6H_4{\cdot}OH\\O{:}CMe{\cdot}C_6H_4{\cdot}OH\end{smallmatrix}$; *o*-hydroxyacetophenone and tin ...tetrachloride form in cold benzene a mixture of the normal additive ...compound and of the substituted compound, which evolves hydrogen ...chloride by warming, and changes entirely to the substituted *compound*, $\begin{smallmatrix}CMe{:}O\\C_6H_4{\cdot}O\end{smallmatrix}>SnCl_3$, yellow crystals, m. p. about 238°.

In a similar manner, *o*-hydroxybenzophenone yields the similarly ...constituted *substance*, $C_6H_4Bz{\cdot}OSnCl_3$, pale yellow leaflets containing ...C_6H_6, m. p. about 250° to a brown liquid; resacetophenone yields ...the *substance*, $OH{\cdot}C_6H_3Ac{\cdot}OSnCl_3$, pale yellow crystals, m. p. ...235—248° to a red liquid (the additive *compound*,

$$2C_6H_3Ac(OH)_2,SnCl_4,$$

is precipitated first, and then changes to the substituted compound; quinacetophenone yields the *substance*, $OH\cdot C_6H_3Ac\cdot OSnCl_2$, deep yellow prisms; euxanthone yields the *substance*,

$$OH\cdot C_6H_3{<}{}^{O}_{CO}{>}C_6H_3\cdot OSnCl_2,$$

orange-yellow crystals; gallacetophenone yields the *substance*,

$$OH\cdot C_6H_2Ac{<}{}^{O}_{O}{>}SnCl_2,$$

deep yellow powder; and gallobenzophenone yields the *substance*, $OH\cdot C_6H_2Bz{<}{}^{O}_{O}{>}SnCl_2$, orange powder containing $\frac{1}{4}$—$\frac{1}{2}C_6H_6$. Of course, in all of these substances the tin is attached co-ordinatively to the carbonyl oxygen atom. C. S.

Aniline Black and its Intermediate Products. ARTHUR G. GREEN and SALOMON WOLFF (*Ber.*, 1911, **44**, 2570—2582).—In connexion with the series of quinonoid derivatives constituting the primary oxidation products of aniline, the various points of controversy between Green and Willstätter appear to turn on the claim of Willstätter and Dorogi (Abstr., 1909, i, 535, 975) that the triquinonoid black is identical with emeraldine [which is diquinonoid according to Green and Woodhead (Trans., 1910, **97**, 2388)], but has the formula of Green and Woodhead's nigraniline; or, generally, the number of quinonoid nuclei in Willstätter's series of primary oxidation products of aniline is one greater than the number in Green's series. Willstätter and Cramer (this vol., i, 90) confirm Willstätter and Dorogi's views by estimating the number of quinonoid nuclei by means of phenylhydrazine at temperatures up to 150°. The authors now show that the phenylhydrazine process, although giving good results below 90°, is quite inaccurate at temperatures above 100°, owing to the spontaneous decomposition of the phenylhydrazine; emeraldine or nigraniline is completely reduced to the leuco-compound by phenylhydrazine at 80—90°, but when this temperature is exceeded a further evolution of nitrogen occurs without any further change in the reduced product.

In the preparation of their quinonoid blacks, Willstätter and Dorogi submit the product to a prolonged treatment with sulphuric acid. The authors condemn this process, since its effect is to convert triquinonoid and tetraquinonoid blacks into a mixture of emeraldine and polymerisation or decomposition products insoluble in 80% acetic acid. Dichromate black, prepared by Willstätter and Dorogi's method, omitting the acid treatment, is identical with Green and Woodhead's emeraldine; it dissolves completely in 80% acetic acid, forming a pale green solution, and yields by treatment with phenylhydrazine at 80—90° a volume of nitrogen corresponding with the diquinonoid formula. The preceding remarks serve to answer most of the recent criticisms of Willstätter and Cramer (this vol., i, 736). Their contention that Green and Woodhead's leucoemeraldine is not the real leuco-base, but is a monoquinonoid black, $C_{48}H_{40}N_8$, is regarded as extremely improbable. C. S.

Dimethylpyrone. ADOLF VON BAEYER and JEAN PICCARD (*Annalen*, 1911, **384**, 208—224).—2 : 4 : 6-*Trimethylpyroxonium perchlorate*, $CMe<\begin{matrix}CH\cdot CMe\\CH:CMe\end{matrix}>O\cdot ClO_4$, colourless, indistinct prisms, m. p. 141—151° (decomp.), is obtained under the following definite conditions. A solution of dimethylpyrone in dry anisole at the ordinary temperature is cooled in a freezing mixture and treated with ethereal magnesium methyl iodide within the course of a minute. After one minute the mixture is added to 20% perchloric acid at −10°, and the perchlorate begins to crystallise almost immediately. 4-*Phenyl*-2 : 6-*dimethylpyroxonium perchlorate*, $C_{13}H_{13}O_5Cl$, sulphur-yellow leaflets, m. p. 210—212° (decomp.), is prepared in a similar manner; the *picrate*, $C_{19}H_{15}O_8N_3$, has m. p. 193°. All pyroxonium salts are converted into the corresponding pyridine compounds by aqueous ammonia in the cold; thus trimethylpyroxonium perchlorate yields 2 : 4 : 6-trimethylpyridine (*perchlorate*, m. p. 243—244°), the methiodide of which is converted by aqueous perchloric acid into 1 : 2 : 4 : 6-*tetramethylpyridinium perchlorate*, $C_9H_{14}O_4NCl$, m. p. 206—207°, which is also produced from trimethylpyroxonium perchlorate and methylamine. Trimethylpyroxonium perchlorate is converted by boiling alcoholic *p*-toluidine into 1-*p*-*tolyl*-2 : 4 : 6-*trimethylpyridinium perchlorate*, $CMe<\begin{matrix}CH\cdot CMe\\CH:CMe\end{matrix}>N(C_7H_7)\cdot ClO_4$, m. p. 141—142°, whilst phenyldimethylpyroxonium perchlorate is converted similarly into 4-*phenyl*-1-*p*-*tolyl*-2 : 6-*dimethylpyridinium perchlorate*, m. p. 205°.

When an aqueous solution of trimethylpyroxonium perchlorate is boiled with barium carbonate in a current of hydrogen, δ-*methyl*-Δγ-*heptene*-βζ-*dione*, COMe·CH·CMe:CH·COMe, is obtained as an unstable oil, which has an odour of peppermint, regenerates the original perchlorate by warming with dilute perchloric acid, and forms a *disemicarbazone*, $C_{10}H_{18}O_2N_6$, m. p. 210—210·5°. δ-*Phenyl*-Δγ-*heptene*-βζ-*dione*, m. p. 51°, obtained in a similar manner from phenyldimethylpyroxonium perchlorate, is an unstable, colourless, crystalline powder. By reduction with palladium chloride and gum arabic in an atmosphere of hydrogen, it yields δ-*phenylheptane*-βζ-*dione*,

$$COMe\cdot CH\cdot CHPh\cdot CH_2\cdot COMe,$$

m. p. 61—62°. δ-*Methylheptane*-βζ-*dione*, b. p. 95—96°/12 mm., obtained in a similar manner, reacts very readily with semicarbazide, forming the *disemicarbazone*, $C_{10}H_{20}O_2N_6$, m. p. 199°. None of these δ-diketones give a reaction with ferric chloride. C. S.

β-Phenylcoumarins. I. GUIDO BARGELLINI and G. LEONARDI (*Gazzetta*, 1911, **41**, i, 737—746).—In the hope of obtaining compounds related to certain substances found in plants, the preparation of some hydroxyl derivatives of β-phenylcoumarin has been undertaken, using an old method for the preparation of coumarin derivatives (compare Komarovski and von Kostanecki, Abstr., 1894, i, 506).

2 : 3 : 4-Trihydroxybenzophenone, when heated for twenty hours with sodium acetate and acetic anhydride, yields the diacetyl-β-phenyldaphnetin of von Kostanecki and Weber (Abstr., 1894, i, 88).

2 : 4-Dihydroxy-4′-methoxybenzophenone (Komarovski and von

Kostanecki, *loc. cit.*) when heated for twenty hours with sodium **acetate and acetic anhydride yields (1) a substance,** probably the *diacetyl* derivative of 2 : 4-dihydroxy-4'-methoxybenzophenone; and (2) an *acetyl* derivative of *4-hydroxy-4'-methoxy-β-phenylcoumarin*, $C_{18}H_{14}O_5$, which forms colourless, woolly needles, m. p. 185—186°. By dissolving this substance in concentrated sulphuric acid and pouring the solution into water, *4-hydroxy-4'-methoxy-β-phenylcoumarin*, $C_{16}H_{12}O_4$, is obtained; it forms yellowish-white needles, m. p. 261—263°. The compound dissolves in alkalis, giving yellow solutions with a green fluorescence; the solution in alcohol is also fluorescent, but the fluorescence disappears on the addition of acid. The substance dissolves in concentrated sulphuric acid, giving a green coloration. When it is treated with methyl iodide, *4 : 4'-dimethoxy-β-phenylcoumarin*, $C_{17}H_{14}O_4$, m. p. 156°, is obtained.

2 : 4 : 4'-Trihydroxybenzophenone yields, when heated with sodium acetate and acetic anhydride, (1) *triacetoxybenzophenone*, which forms colourless needles, m. p. 96—98°; (2) *4 : 4'-diacetoxy-β-phenylcoumarin*, $C_{19}H_{14}O_6$, which crystallises in colourless needles, m. p. 189—190°. *4 : 4'-Dihydroxy-β-phenylcoumarin*, $C_{15}H_{10}O_4$, prepared from it, forms yellowish-white needles, m. p. 238—240°. When treated with methyl iodide, it yields 4 : 4'-dimethoxy-β-phenylcoumarin, previously described.

R. V. S.

β-Phenylcoumarins. II. GUIDO BARGELLINI and G. FORLI FORTI (*Gazzetta*, 1911, **41**, i, 747—756. Compare preceding abstract. —The synthesis of β-phenylcoumarins has been continued by another method (compare von Kostanecki and Weber, Abstr., 1894, i, 88), namely, the condensation of *p*-cyanoacetylanisole or cyanoacetylveratrole (1 : 2-dimethoxy-4-cyanoacetophenone) with resorcinol or phloroglucinol.

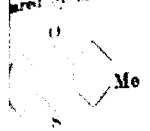
p-*Cyanoacetylanisole*, $C_{10}H_9O_2N$ (from *p*-chloroacetylanisole and potassium cyanide), crystallises in tufts of long, colourless needles, m. p. 128—130°. When it is heated with resorcinol and 73% sulphuric acid on the water-bath, two products are obtained: (1) a *substance*, soluble in water, which forms colourless needles, m. p. 234—236°, and is probably the nitrile or amide of the coumarin derivative, m. p. 260—262°, which it yields on addition of hydrochloric acid; (2) 4-hydroxy-4'-methoxy-β-phenylcoumarin, m. p. 260—262°, identical with that described in the preceding abstract.

Condensation of *p*-cyanoacetylanisole with phloroglucinol yields a *substance*, m. p. about 200°, from which an *acetyl* derivative can be prepared, which crystallises in colourless needles, m. p. 179—180°.

Chloroacetylveratrole can be obtained: (1) by the action of methyl sulphate on chloroacetylcatechol; and (2) by condensation of chloroacetyl chloride with veratrole in presence of aluminium chloride. In the second case another substance (? *chloroacetylguaiacol*) is the principal product; in both cases the yield is exceedingly small. *Chloroacetylveratrole*, $C_{10}H_{11}O_3Cl$, crystallises in white scales, m. p. 102—104°. *Cyanoacetylveratrole*, $C_{11}H_{11}O_3N$, forms colourless needles, m. p. 134—135°. With resorcinol in presence of 73% sulphuric acid, it yields a *substance*, which crystallises in yellowish-

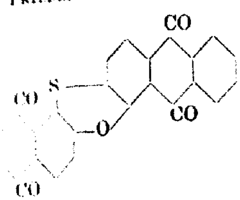
white needles, m. p. 228—229°, whilst with phloroglucinol a reddish-yellow condensation product is obtained. R. V. S.

Preparation of Phenothioxin and its Derivatives. AKTIEN-GESELLSCHAFT FÜR ANILIN-FABRIKATION (D.R.-P. 234743).—It is found that the phenothioxin, m. p. 60—61°, b. p. 183—184°/12 mm., prepared by Mauthner (Abstr., 1906, i, 448) can be readily obtained by heating (with continual stirring) phenyl ether at 60—70° with sulphur in the presence of aluminium chloride; the temperature is subsequently slowly raised to 100° and maintained until evolution of hydrogen sulphide ceases. Under these conditions, *p*-tolylphenyl ether yields 3-*methylphenothioxin* (annexed formula), m. p. 36°, b. p. 185—187°/12 mm., whilst *p*-chlorophenyl ether furnishes 3-*chlorophenothioxin*, m. p. 37°, b. p. 176°/12 mm.



F. M. G. M.

Preparation of Anthracene Derivatives. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235094).—When anthraquinone-1-thiol is heated with 1-hydroxyanthraquinone at 160—170° in 98% sulphuric acid, it yields a *compound* (annexed formula), which crystallises from hot quinoline in brownish-red needles. The tinctorial properties of this and the following analogous condensation products are tabulated in the original.



1 : 5-Dithiolanthraquinone with 1- and 2-hydroxyanthraquinones (2 mols.) respectively; 1-thiolanthraquinone (2 mols.) and anthrarufin; 1-thiol-5-aminoanthraquinone and 5-amino-1-hydroxyanthraquinone; 1-thiolanthraquinone with 2-hydroxyanthraquinone; and 1-thiolanthraquinone (2 mols.) with anthraflavic acid; 2-thiolanthraquinone (1 mol.) with 2-hydroxyanthraquinone and (2 mols.) with anthraflavic acid. F. M. G. M.

Solubility of Alkaloids in an Aqueous Boric Acid-Glycerol Solution. E. BARONI and O. BORLINETTO (*Chem. Zentr.*, 1911, ii, 93—94; from *Giorn. Farm. Chim.*, 1911, **60**, 193—195).—A solution containing 3·0 grams of boric acid, 50·0 grams of glycerol, and water to 100 c.c., dissolves the following quantities of various alkaloids, the figures in parentheses giving the solubility of the respective alkaloids in water: Codeine, 4% (1·66%); atropine, 10% (0·5%); cocaine, 8% (0·14%); morphine, 5·5% (0·1%); strychnine, 3·5% (0·01%); eserine, 7·5% (trace); veratrine, 6% (trace). The solubility of the alkaloids increases with the proportion of boric acid present in the solution. W. P. S.

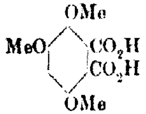
Crystalline Alkaloid of Calycanthus glaucus. IV. Some Salts of a New Quaternary Base obtained by Methylating *iso*Calycanthine. HARRY M. GORDIN (*J. Amer. Chem. Soc.*, 1911, **33**, 1626—1632).—When *iso*calycanthine (Abstr., 1910, i, 62) is treated

with methyl iodide, about 35% of the alkaloid is converted into the hydriodide, about 35% remains unchanged, and the remainder is converted into a quaternary iodide, $C_{24}H_{28}ON_3I,H_2O$. It is suggested **that the oxygen of the air takes part in the reaction, as** shown by the **equations:** $2C_{11}H_{14}N_2 + 2MeI + O_2 = C_{24}H_{28}ON_3I,H_2O + NH_4I$ and $C_{11}H_{14}N_2 + NH_4I = C_{11}H_{14}N_2,HI + NH_3$.

The quaternary *iodide* forms white, flat, lustrous needles, becomes brown at 213—214°, does not melt below 325°, and is soluble in about 30 parts of hot methyl alcohol; its ***hydriodide*** is described. The corresponding ***chloride***, $C_{24}H_{28}ON_3Cl,3H_2O$, m. p. 220°, crystallises in flat, lustrous needles, and is soluble in about 50 parts of cold water; its ***hydrochloride*** is described. The ***nitrate***, $C_{24}H_{28}ON_3 \cdot NO_3$, m. p. 192—194°, forms white, rectangular prisms. The quaternary picrate, m. p. 155°, and ***picrolonate***, m. p. 164—166°, are also described.

F. G.

Colchicine. I. and II. ADOLF WINDAUS (*Chem. Zentr.*, 1911, i, 1637—1638, 1638—1641; from *Sitzungsber. Heidelberger Akad. Wiss.*, 1910, 1—7; 1911, 1—27).—On oxidation of colchicine in potassium hydroxide with potassium permanganate, in addition to oxalic acid, ***trimethoxy-o-phthalic acid***, $C_{11}H_{12}O_7$, is obtained, which must have the annexed structure, since it differs from the trimethoxygallocarboxylic acid described by Feist.



By cautious sublimation of the reaction product in a vacuum at 220°, the *anhydride*, $C_{11}H_{10}O_6$, is obtained in needles, m. p. 143—144°. This is converted into the acid when boiled with water, which crystallises in transparent plates, m. p. 175—176°; the *silver* and *lead* salts are insoluble; the *barium* salt forms needles. The *anil* crystallises in colourless needles, m. p. 16[illegible].

Derivatives of Trimethylcolchicinic Acid.—Colchicine was regarded by Zeisel as the methyl ester of an acid, colchiceine, but it is now considered to be an enolic methyl ether, colchiceine being an enol, since it gives a characteristic green coloration with ferric chloride. Zeisel has shown further, that colchiceine contains an acetyl group attached to nitrogen, so that the structure of colchicine may be expressed $C_6H(OMe)_3{:}C_{10}H_8O(OMe)\cdot NH\cdot COMe$.

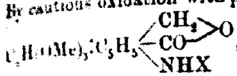
The almost colourless aqueous or alcoholic solutions of colchicine and its derivatives become deep yellow on the addition of hydrochloric acid, owing to the formation of acid additive products. ***Trimethylcolchicinic acid dihydrochloride***, $C_{19}H_{21}O_5N,2HCl,H_2O$, forms dark yellow crystals; it still contains the free enolic group, and when heated at 100°, regenerates the monohydrochloride. ***Trimethylcolchicinic acid dibenzoate***, $C_6H(OMe)_3{:}C_{10}H_8O(O\cdot COPh)\cdot NH\cdot COPh$, crystallises in faint yellow, three-sided prisms, m. p. 298° (decomp.); it gives no coloration with ferric chloride. N-***Benzoyltrimethylcolchicinic acid***, $C_6H(OMe)_3{:}C_{10}H_8O(OH)\cdot NH\cdot COPh$, prepared by heating the dibenzoate with 25% potassium hydroxide, separates in pale yellow needles, m. p. 253—254°, and gives a dark green ferric chloride coloration.

N-p-*Nitrobenzoyltrimethylcolchicinic acid* forms prisms, m. p. 256°. N-p-*Bromobenzoyltrimethylcolchicinic acid* separates in platelets, m. p. 25[illegible]. N-*Benzenesulphonyltrimethylcolchicinic acid*,

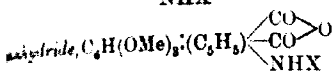
$C_6H(OMe)_3{:}C_{10}H_8O(OH){\cdot}NH{\cdot}SO_2Ph$,

forms greenish-yellow, rhombic plates, m. p. 255°, and gives an intense green ferric chloride reaction. *Trimethylcolchicinic acid dibenzenesulphonate*, prepared by the action of benzenesulphonyl chloride on the hydrochloride in pyridine solution, crystallises in yellow, four-sided, rhombic plates, m. p. 196°. The mother liquors contain an isomeric *benzenesulphonate*, crystallising in greenish-yellow prisms and plates, m. p. 141—142°. Neither isomeride gives any coloration with ferric chloride, and they are regarded as cis-, trans-isomerides.

Oxidation of Colchicine Derivatives with Potassium Permanganate.—By cautious oxidation with potassium permanganate, a lactone, *colchide*,

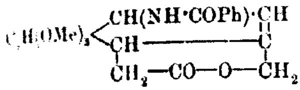


, and an acid anhydride, *colchinic anhydride*,

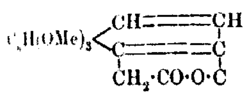


, have been obtained.

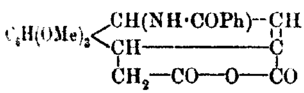
N-*Benzoylcolchide*, $C_{23}H_{23}O_6N$ (annexed formula), formed on oxidation of N-benzoyltrimethylcolchicinic acid, forms needles, m. p. 239°, $[\alpha]_D^{17}$ −275°; it gives no coloration with ferric chloride, and is neutral towards litmus paper.



On further oxidation trimethoxyphthalic acid is formed. It dissolves in alcoholic potassium hydroxide, the equilibrium between hydroxy-acid and lactone depending on the amount of alkali present. When heated for two hours at 250° under diminished pressure, benzamide and *trimethoxyhomonaphthide*, $C_{16}H_{16}O_5$, are obtained. The latter (annexed formula) crystallises in needles, m. p. 138°, is optically inactive, and behaves as a lactone; it is also formed on boiling N-benzoylcolchide with alcoholic hydrogen chloride, whereby, in part, benzoic acid and the corresponding amine, colchide, are formed; *colchide picrate*, $C_{16}H_{19}O_5N,C_6H_3O_7N_3$, crystallises in yellow prisms, m. p. 165°.



N-*Benzoylcolchinic anhydride* (annexed formula), prepared by oxidation of N-benzoyltrimethylcolchicinic acid, forms straggling, four-sided platelets, m. p. 207°, $[\alpha]_D^{18}$ −288°. The solutions in water and organic solvents are intense yellow, but the alkali salt solutions are colourless and remain so at first on the addition of acid; later they become yellow, and the anhydride crystallises. The *anil*, $C_{29}H_{26}O_6N_2$, forms almost colourless needles, m. p. 226°.



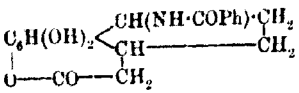
On heating with zinc dust and acetic acid, a tetrahydronaphthalene

derivative, $C_{23}H_{23}O_8N$, probably having the formula

$$C_6H(OMe)_3<\begin{matrix}CH(NH\cdot COPh)\cdot CH_2 \\ CH_2(CH_2\cdot CO_2H)\cdot CH\cdot CO_2H\end{matrix}$$

is obtained; it separates in colourless needles, m. p. 158° after previously sintering.

When the anhydride is warmed with hydriodic acid, the methyl groups and carbon dioxide are eliminated, and a compound, $C_{19}H_{17}O_5N$, having possibly the annexed formula is obtained; it crystallises in colourless needles, which darken at 200°, decomp. 230°.



The reasons for assigning the formula given to benzoylcolchinic anhydride are discussed at length.

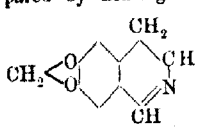
N-*Acetylcolchide* forms needles, m. p. 221°; the lactone ring is only opened with difficulty.

N-*Acetylcolchinic anhydride* forms deep yellow needles, m. p. 2[illegible]°, and dissolves without colour in alkali hydroxides.

N-*Benzenesulphonylcolchinic anhydride*, $C_{28}H_{21}O_8NS$, crystallises in long, four-sided plates, m. p. 242—243° (decomp.). When hydrolysed and again acylated, it is converted into *N*-benzoylcolchinic anhydride.

E. F. A.

Preparation of Hydrastinine Salts. HERMAN DECKER (D.R.-P. 234850. Compare Abstr., 1908, i, 901).—When *formylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NH\cdot COH$, needles, m. p. 51—52°, prepared by heating homopiperonylamine formate at 160—170°, is heated with phosphoric oxide, it yields 6 : 7-*methylenedioxy*-3 : 4-*dihydro*iso*quinoline* (annexed formula), nodular crystals, m. p. 50—[illegible]°; its salts exhibit blue fluorescence, and the *picrate* has m. p. 238°; on treatment with methyl iodide, it furnishes hydrastinine hydriodide, and with methyl sulphate yields *hydrastinine methosulphate*, a yellow powder, m. p. 117—119°; the *picrate* has m. p. 175°.



F. M. G. M.

Action of Organic Magnesium Compounds on Hydrastinine. MARTIN FREUND and KARL LEDERER (*Ber.*, 1911, 44, 2356—236[illegible]).—Hydrastinine interacts with organo-magnesium compounds in a similar manner to cotarnine (Freund and Reitz, Abstr., 1906, i, [illegible]), forming α-alkylhydrohydrastinine compounds of the type

$$CH_2O_2<\begin{matrix}C{:}CH\cdot C\cdot CHR\cdot NMe \\ C{:}CH\cdot C\cdot CH_2-CH_2\end{matrix};$$

these are 1-alkyltetrahydro*iso*quinoline derivatives. Free hydrastinine gives a 50% yield; the hydrochloride reacts quantitatively with the Grignard reagent.

α-*Methylhydrohydrastinine* is an oil; the *hydriodide* crystallises in plates, m. p. 227°; the *methiodide* also forms plates, m. p. 229—230°.

α-*Ethylhydrohydrastinine* crystallises in hard, colourless plates, m. p. 70—71°.

α-*Phenylhydrohydrastinine* + H_2O forms long, pointed crystals, m. p. [illegible]°; the anhydrous substance forms a yellow, resinous mass.

α-*Propylhydrohydrastinine* is oily; the *hydriodide* crystallises in plates, m. p. 185—186°; the *platinichloride* forms rhombic crystals, decomp. 230°; the *methiodide* separates in plates, which sinter at 163°, m. p. 168—169°.

*iso*Propylhydrohydrastinine is likewise oily. The *hydrobromide* crystallises in pointed needles, m. p. 190°; the *hydriodide* forms colourless, rhombic plates, m. p. 217—218°; the *picrate* forms plates, m. p. 143—145°; the *platinichloride* separates in needles, m. p. 223°; the *methiodide* forms bunches of needles, m. p. 219—220°.

α-*Butylhydrohydrastinine* is oily; it is characterised by the *picrate*, plates, m. p. 147—148°; the *platinichloride*, rhombic plates, m. p. 222—223°, and the *methiodide*, leaflets, m. p. 205—206°.

α-*iso*Butylhydrohydrastinine gives a *picrate*, crystallising in prisms, which sinter at 125°, m. p. 130°; a *platinichloride*, separating in four-sided plates, decomp. 220°, and a *methiodide*, which forms bunches of leaflets, m. p. 197—198°.

α-*Benzylhydrohydrastinine* is an oil, but forms crystalline salts. The *hydrochloride* forms six-sided crystals, m. p. 182°; the *hydrobromide* has m. p. 187—188°; the *hydriodide* crystallises in hexagonal plates, m. p. 195—196°; the *acid sulphate* sinters at 185°, m. p. 189°; the *picrate* forms octahedra, m. p. 178—180°; the *platinichloride* forms plates, decomp. 224°, whilst the *methiodide* forms aggregates of columnar crystals, m. p. 245°.

α-p-*Anisylhydrohydrastinine* crystallises in columns united in bundles, m. p. 98—99°; the *hydrochloride* forms needles; the *hydrobromide* is similar, m. p. 243—244°; also the *hydriodide*, m. p. 223—224°.

α-*Naphthylhydrohydrastinine* forms rhombic plates, which sinter at 125°, m. p. 127—128°. The *hydrochloride*, m. p. 254—255°; the *hydrobromide*, needles, m. p. 265°; the *hydriodide*, needles, m. p. 262°; the *acid sulphate*, matted crystals, which sinter at 225°, m. p. 228—229° (decomp.), and the *picrate*, plates, decomp. 201°, are described.

E. F. A.

Formation of Alkaloidal Periodides. W. C. Holmes (*Philippine J. Sci.*, 1911, *A*, **6**, 253—275).—A résumé of the literature relating to the formation of alkaloidal periodides and the use of these compounds in the estimation of alkaloids is given. It is shown that morphine, codeine, and heroine, free or in the form of salts, have a remarkable affinity for iodine, and readily combine with it even in the absence of a solvent. There is no tendency to form definite compounds. The reactions are apparently dependent on the concentration of the iodine, and the phenomena observed are those of equilibrium involving vapour and osmotic pressures as factors. The amount of "free" iodine combined with the alkaloids cannot be determined by thiosulphate solution, and consequently it is considered that the formation and constitution of the periodides are much more complex than has been supposed.

When $N/10$-iodine solution is added to a 1% solution of codeine,

morphine, or heroine sulphate in $N/10$-sulphuric acid, and the uncombined iodine titrated wth $N/10$-sodium thiosulphate after standing overnight, the amounts of iodine absorbed by the alkaloids increase with the total concentration of iodine in the mixed solutions, but a maximum is soon reached in the case of heroine. When other factors are varied and the concentration of iodine and alkaloid kept constant, the amount of iodine absorbed varies inversely with rise in temperature, or increase in concentration of (*a*) sulphuric acid, (*b*) potassium iodide. Equilibrium appears to be reached in about thirty minutes. All the codeine precipitates were crystalline, as were also two of the morphine precipitates, whilst with heroine only amorphous deposits were obtained. The belief that in using Wagner's reagent for the estimation of alkaloids a definite amount of iodine combines with the alkaloid and may be determined by titration of the residual iodine is fallacious (compare Prescott and Gordin, Abstr., 1899, i, 89).

Aqueous solutions of free morphine, codeine, and heroine are precipitated by Wagner's reagent, and here, also, the amount of iodine absorbed is proportional to the concentration of iodine, and is inversely proportional to the amount of acid, which may be added subsequently. The free alkaloids and their sulphates also absorb iodine vapour when exposed to it, the salts being distinctly less active than the free bases.

T. A. H.

Methylation of the Alcoholic Hydroxyl Group in Morphine, Codeine, and the Methylmorphimethines. Roland Pschorr and F. Dickhäuser [and, in part, C. D'Avis] (*Ber.*, 1911, **44**, 2633—2640).—The alkylation of the alcoholic hydroxyl group in morphine, which has not hitherto been effected, proceeds quite easily in the cold when the alkaloid is shaken with methyl sulphate or methyl iodide and N-sodium hydroxide ($2\frac{1}{2}$ mols.). The product of the reaction, which is also obtained by starting with codeine, is precipitated by concentrated potassium iodide, whereby *methylcodeine methiodide*, decomp. 257° (corr.), $[\alpha]_D^{23}$ $-107{\cdot}2°$ in water, is obtained. A boiling aqueous solution of the methiodide is converted by 25% sodium hydroxide into *α-dimethylmorphimethine*, $C_{20}H_{25}O_3N$, leaflets or needles, m. p. 94°, $[\alpha]_D^{24}$ $-201{\cdot}7°$ in methyl alcohol (*methiodide*, $C_{21}H_{28}O_3NI$, decomp. 256° (corr.), $[\alpha]_D^{23}$ $-134{\cdot}4°$ in water), which is changed by heating with aqueous alcoholic potassium hydroxide or with acetic anhydride at 210° to *β-dimethylmorphimethine*, isolated in the form of the *methiodide*, $C_{21}H_{28}O_3NI$, prismatic needles, decomp. 318—320° (corr.), $[\alpha]_D^{23}$ 268·5—278·5° in water.

The methylation of α- and β-methylmorphimethine is effected as in the case of morphine or codeine, the methiodides obtained being identical with those of α- and β-dimethylmorphimethine mentioned above. *γ-Dimethylmorphimethine methiodide*, $C_{21}H_{28}O_3NI$, leaflets, has decomp. 259° (corr.) and $[\alpha]_D^{20}$ $+14°$ in water. *δ-Dimethylmorphimethine methiodide*, needles, has decomp. 286° (corr.), and $[\alpha]_D^{23}$ 170·9° in water. *ε-Dimethylmorphimethine methiodide*, long needles, has decomp. 277° (corr.), and $[\alpha]_D^{20}$ $-79{\cdot}4°$ in methyl alcohol.

β-Dimethylmorphimethine methiodide is decomposed by aqueous

alcoholic potassium hydroxide at 165°, forming morphenol, ethylene, and trimethylamine.

The methylation of various alcohols by sodium hydroxide and methyl sulphate has been examined. The method yields good results with benzyl alcohol and cinnamyl alcohol, but is unsatisfactory with *iso*-amyl alcohol, octyl alcohol, borneol, and *iso*borneol. C. S.

Codeine Oxide. MARTIN FREUND and EDMUND SPEYER (*Ber.*, 1911, 4, 2339—2353. Compare this vol., i, 76).—When codeine oxide, dissolved in acetic anhydride, reacts with sulphuric acid, two isomeric substances, $C_{18}H_{20}O_7NS$, are formed, both of which are acid in character, codeineoxidesulphonic acid (I.) and α-codeineoxidesulphonic acid (II.), these probably have the annexed constitutions; the α compound is

$$(I.)\quad [C_{18}H_{20}O_3]\lessgtr^{SO_3H}_{N:O} \qquad (II.)\quad [C_{18}H_{20}O_3]\lessgtr^{SO_2-}_{N(OH)}>O$$

easily converted into the isomeride.

On reduction, both are converted into the same codeinesulphonic acid, $N\vdots[C_{18}H_{20}O_3]\cdot SO_3H$. This, on treatment with nitric acid, yields the nitrocodeine described by Anderson. Proof that no change in the structure of the alkaloid complex has taken place is afforded by the fact that all the sulphonic acids described yield codeine when superheated with water. When dissolved in cold concentrated sulphuric acid, the sulphonic acids, however, are more profoundly altered, and new products are obtained which await further investigation.

Codeinesulphonic acid when treated with methyl iodide in alkaline solution forms codeinesulphonic acid methyl hydroxide,

$$NMe\colon[C_{18}H_{20}O_3](OH)\cdot SO_3H.$$

On boiling with alkali, βγ-dimethylbutylene-βγ-diamine is eliminated and a nitrogen-free product obtained, which could not be isolated. After remaining in alkaline solution with methyl iodide and alcohol for some time and then boiling, the methyl hydroxide is converted into a crystalline salt, $C_{16}H_{11}O_6SK$, which is regarded as a morphenol derivative, $O\colon C_{14}H_5(OMe)_2\cdot SO_3K$.

α-Codeineoxidesulphonic acid behaves in many respects otherwise than the isomeride. With nitric acid a nitro-compound,

$$O\colon N\vdots[C_{18}H_{19}O_3](NO_2)\cdot SO_3H,$$

is obtained. Sulphurous acid converts this into a nitrocodeine isomeric with Anderson's, but both isomerides give the same aminocodeine when reduced.

When α-codeineoxidesulphonic acid is treated with bromine water, and the perbromide formed is boiled with alcohol, a compound, $C_{15}H_{17}O_4Br_3$ or $C_{15}H_{15}O_4Br_3$, is obtained of unknown constitution.

Morphine oxide, when similarly treated with acetic anhydride and sulphuric acid, forms a bimolecular hydroxysulphonic acid, $C_{34}H_{40}O_{15}N_2S_2$, which is converted by sulphurous acid into a compound, $C_{17}H_{21}O_7NS$.

Codeineoxidesulphonic acid forms small crystals of the hexagonal system, decomp. 272°, $[\alpha]_D$ −115·4°, and forms a crystalline *potassium* salt.

Codeinesulphonic acid is dimorphous, crystallising in well-formed prisms and silky needles, which can be converted into one another. It decomposes above 300° and has $[\alpha]_D$ −136·3°.

Codeinesulphonic acid methylhydroxide separates in needles, decomp. 284°, $[\alpha]_D$ −63·2°. Treatment with methyl iodide and alcohol and subsequent boiling with alkali gives a *compound*, $C_{16}H_{11}O_6SK$, crystallising in well-formed plates, decomp. 295°. On treatment of codeineoxidesulphonic acid with cold concentrated sulphuric acid, a substance, $C_{18}H_{21}O_8NS$, provisionally termed *β-codeinesulphonic acid*, is obtained. It forms bundles of microscopic plates, decomp. 243°, $[\alpha]_D$ −19[illegible]. Sulphurous acid converts this into an isomeric substance, provisionally termed *γ-codeinesulphonic acid*, which crystallises in matted needles, decomp. 280°.

Potassium chromate oxidises codeineoxidesulphonic acid into *codeineoxidesulphonic acid hydrate*, $C_{18}H_{23}O_8NS$, crystallising in needles; on heating at 180° with water under pressure, a *base* separating in stunted, prismatic plates or long needles, m. p. 180°, is obtained; the *hydrochloride* forms long needles, m. p. 310°.

Concentrated sulphuric acid converts codeinesulphonic acid into a *compound*, $C_{19}H_{18}O_3N{\cdot}SO_3H$, which crystallises in very slender needles, decomp. 285—290°.

a-Codeineoxidesulphonic acid crystallises in stunted prisms; it is converted into the isomeride on heating with 10% sodium hydroxide or 20% hydrochloric acid.

Nitro-a-codeineoxidesulphonic acid crystallises in yellow plates, decomp. 167—170°.

a-Nitrocodeine, prepared by the action of sulphurous acid on the sulphonic acid, crystallises in microscopic, four-sided plates, m. p. 19[illegible].

By the interaction of bromine and a-codeineoxidesulphonic acid, a *compound*, $C_{15}H_{17}O_4Br_3$, is obtained in long needles, m. p. 258—2[illegible] (decomp.).

Codeinesulphonic acid is without physiological action.

Both the isomeric nitrocodeines when reduced electrolytically yield the same *aminocodeine*, $C_{18}H_{20}O_3N{\cdot}NH_2$, crystallising in plates, m. p. 228°. The *hydrochloride* forms needles, m. p. 290°.

Hydroxycodeine, prepared by diazotisation of aminocodeine and boiling, crystallises in colourless plates, which when heated lose water at 176—185°, m. p. 234°. The *hydrochloride* crystallises in needles.

E. F. A.

Cotarnine. VI. MARTIN FREUND and KARL LEDERER (*Ber.*, 1911, **44**, 2353—2356).—Tarconine methiodide reacts with magnesium phenyl iodide, forming *8-methoxy-6 : 7-methylenedioxy-1-phenyl-2-methyl-1 : 2-dihydroisoquinoline*, $CH_2{<}\begin{matrix} O{\cdot}C{:}C(OMe){\cdot}C{\cdot}CHPh{\cdot}NMe \\ O{\cdot}C{:}CH{-\!\!-\!\!-}C{\cdot}CH{=}CH \end{matrix}$. On reduction this is converted into a-phenylhydrocotarnine (8-methoxy-6 : 7-methylenedioxy-1-phenyl-2-methyltetrahydro*iso*quinoline), previously prepared by Freund and Reitz (Abstr., 1906, i, 600) from cotarnine salts and magnesium phenyl iodide.

a-Phenyltarconine forms colourless bunches of pointed crystals, which sinter at 97°, m. p. 102°. The salts and methiodide are oily, and decompose with a red coloration.

a-Butylhydrocotarnine, $CH_2O_2{<}\begin{matrix} C{:}C(OMe){\cdot}C{\cdot}CH(C_4H_9){\cdot}NMe \\ C{:}CH{-\!\!-\!\!-}C{\cdot}CH_2{-\!\!-\!\!-}CH_2 \end{matrix}$, pre-

…ared from cotarnine hydrochloride and magnesium butyl bromide is an oil. The following crystalline salts have been analysed: *hydrochloride*, plates, m. p. 215—216°; *hydrobromide*, plates, m. p. 207—208°; *hydriodide*, columns, m. p. 190—191°; *picrate*, plates, m. p. 165—166°; *platinichloride*, plates, m. p. 205—206°; *methiodide*, long, rhombic plates, m. p. 190—193°.

E. F. A.

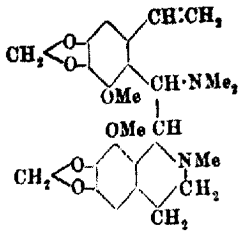
Stereochemistry of Nitrogen Compounds. Isomeric Bis-hydrocotarnines. MARTIN FREUND and OTTO KUPFER (*Annalen*, 1911, 384, 1—38).—Bis-hydrocotarnine (di-hydrocotarnine) has been prepared by Freund and Reitz (Abstr., 1906, i, 600), and the constitution ascribed to it by these authors has been confirmed by Freund and Lederer (see Lederer, *Diss.*, Giessen, 1909) and yet again by the present authors, who have oxidised the substance to cotarnine nearly quantitatively by dilute sulphuric acid and 10% potassium dichromate. From its constitution (the molecule consists of two structurally identical halves, each containing an asymmetric carbon atom) it is obvious that a stereoisomeride should exist, and, indeed, a repetition of Freund and Reitz's experiment has shown that, in addition to the bis-hydrocotarnine already isolated, a small quantity of the isomeride, *iso-bishydrocotarnine*, $C_{24}H_{28}O_6N_2$, is formed. The two compounds have the same m. p., 163—164° (when mixed m. p. about 20° lower), but show marked dissimilarities in the solubilities of their salts; they are easily separated almost quantitatively by means of their *hydrogen sulphates*, that of bishydrocotarnine being very sparingly soluble in dilute sulphuric acid. Bishydrocotarnine forms a dihydrochloride, m. p. 231—232°, dihydrobromide, decomp. 228—229°, dihydriodide, m. p. 228—230°, *dihydrofluoride*, m. p. 227—229°, and *dinitrate*, m. p. 169—171°, whilst *iso*-bishydrocotarnine forms corresponding salts having the same m. p. (the mixed m. p. is always lower). It is changed to bishydrocotarnine at 160°, and gives a quantitative yield of cotarnine by oxidation with potassium dichromate and sulphuric acid.

Possibly bishydrocotarnine and *iso*bishydrocotarnine represent racemic and meso-modifications. However, all attempts to resolve either of them having been unsuccessful, this problem has been put aside for the present, although the suggestion is advanced that the two substances may be cis- and trans-modifications of the meso-form, as in the case of coniine and *iso*-coniine. *iso*-Bishydrocotarnine forms a *methiodide*, $C_{24}H_{28}O_6N_2,MeI$, m. p. 233°. The fact that bishydrocotarnine forms only a monomethiodide (*loc. cit.*) is due to steric hindrance, because when the methiodide is converted into the corresponding *hydroxide*, $C_{24}H_{28}O_6N_2,MeOH,10H_2O$, m. p. 75—80°, and this is treated with methyl iodide, the *methiodide*,

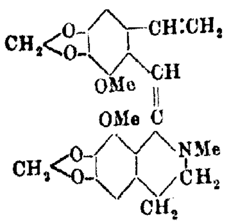
$$C_{24}H_{28}O_6N_2,MeOH,MeI,$$

m. p. 215—216°, is obtained, which is converted by acetic acid and potassium iodide into *bishydrocotarnine dimethiodide* $C_{24}H_{28}O_6N_2,2MeI$, m. p. 201—202°.

When treated with silver oxide and water and subsequently boiled with concentrated potassium hydroxide, bishydrocotarnine methiodide and *iso*-bishydrocotarnine methiodide yield respectively *de-N-methylbis-hydrocotarnine*, $C_{25}H_{30}O_6N_2$, m. p. 120—122° (*dihydriodide*, m. p.

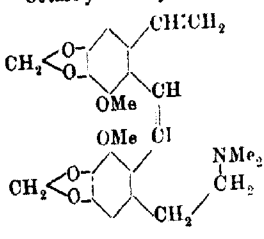


173—175°) and *de-N-methyliso-bishydrocotarnine*, m. p. 136° (*dihydriodide*, m. p. 146—149°), which are regarded as structural isomerides on account of their different chemical behaviour. Although their constitutions have not been definitely settled, that annexed is ascribed to de-*N*-methylbishydrocotarnine, because the substance reacts with bromine to form an additive compound, $C_{25}H_{30}O_6N_2Br_2$, m. p. 164—166°, which contains only one ionisable bromine atom. Both substances yield cotarnine by oxidation, and form only monomethiodides. *De-N-methylbishydrocotarnine methiodide*, $C_{25}H_{30}O_6N_2,MeI$,

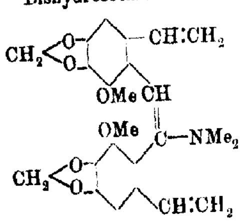


m. p. 151°, is decomposed by alcoholic sodium ethoxide yielding trimethylamine and *cotarnylidenehydrocotarnine* (annexed formula), m. p. 100—102° (decomp.). *De-N-methylisobishydrocotarnine methiodide*, $C_{25}H_{30}O_6N_2,MeI$, m. p. 159—162°, reacts with silver oxide and water and subsequently with potassium hydroxide to form a substance called *bis-de-N-methylisobishydrocotarnine*, $C_{26}H_{32}O_6N_2$, m. p. 218—220° (*hydriodide*, decomp. 248°), the *methiodide*, $C_{26}H_{32}O_6N_2,MeI$, m. p. 156—158°, of which is decomposed by sodium ethoxide, yielding trimethylamine and *cotarnylidene-de-N-methylhydrocotarnine* (see below).

Cotarnylidenehydrocotarnine yields cotarnine by oxidation, and forms with methyl iodide a substance, $C_{24}H_{26}O_6NI$, m. p. 115—117°, called *cotarnylidene-de-N-methyliodohydrocotarnine* (probable constitution annexed), which has pronounced basic properties (*hydriodide*, m. p. 209—211°), and yields by the evaporation of its solution in 50% alcohol the corresponding hydroxy-compound, *cotarnylidene-N-methylhydroxycotarnine*, $C_{24}H_{27}O_7N$, m. p. 73—75° (*methiodide*, m. p. 160—162°).



Bishydrocotarnine dimethiodide, by treatment with silver oxide and water, and subsequently with boiling potassium hydroxide, yields *bis-de-N-methylbishydrocotarnine*, $C_{26}H_{32}O_6N_2$, m. p. 118—120° (*hydrobromide*, m. p. 166—168°; *hydriodide*, m. p. 160—162°), the *methiodide*, m. p. 113—115°, of which yields trimethylamine and *cotarnylidene-de-N-methylhydrocotarnine* (annexed formula), m. p. 68—71°, by treatment with alcoholic sodium ethoxide. The last-mentioned derivative does not react with methyl iodide.



A table is given showing the genetic relations of the preceding substances. C. S.

Alkaloids of Pareira Root. MAX SCHOLTZ (*Arch. Pharm.* 1911, 249, 408—418. Compare Abstr., 1896, i, 710; 1899, i, 92; 1907, i, 79).—It has been shown already (*loc. cit.*) that pareira root contains either *l*- or *d*-bebeerine. A second alkaloid, chondrodine, has now been isolated from the total alkaloids of the root, and this paper deals with the isolation and characterisation of this substance, which may be regarded provisionally as a hydroxybebeerine.

Chondrodine, $C_{18}H_{21}O_4N$, m. p. 218—220°, $[\alpha]_D$ −75° in alcohol, was obtained as an amorphous substance by a complicated process of separation from that portion of the total alkaloids which was insoluble both in ether and chloroform. The *hydrochloride*, B,HCl, m. p. 274—275°, crystallises in yellow leaflets; the *mercurichloride*, m. p. 288—290° (decomp.), is a crystalline powder; the *ferrichloride*, B,HCl,$FeCl_3$, m. p. 183—184°, occurs in microscopic crystals (?); the *perchlorate*, m. p. 232—233°, crystallises from hot water; the *picrate*, m. p. 193—194°, is a greenish-yellow, crystalline powder, and the *picrolonate*, m. p. 185—186°, forms greenish-yellow, stellate clusters of needles. The *methiodide*, m. p. 273° (decomp.), crystallises from water. The alkaloid contains a methoxyl and an :NMe group. With acetic anhydride at 50—60° it furnishes an amorphous *diacetyl* derivative, which blackens above 270°. The *dibenzoyl* compound, m. p. 295°, separates from hot alcohol in crystalline granules. When heated with ethyl iodide in presence of alcohol and potassium hydroxide, chondrodine furnishes a *diethyl ether*, m. p. 205—207°, as a yellowish-white, sandy powder: the *hydrochloride* of this forms yellow needles and melts at 258°.

Bebeerine methiodide on further treatment with methyl iodide yields a *methyl ether*, $C_{16}H_{14}O(OMe)_2\cdot NMe_2I$, m. p. 263—264°, which separates from water as a yellow, crystalline powder. *Ethyl bebeerine*, m. p. 150°, obtained by the action of ethyl iodide on bebeerine in presence of potassium hydroxide and alcohol, is a colourless powder, soluble in alcohol, but not in ether; it is lævorotatory, $[\alpha]_D = -250°$ in alcohol, gives a crystalline *hydrochloride*, yellow leaflets, m. p. 109—110°, and furnishes a *methiodide*, m. p. 255—256°, which crystallises from hot water in needles. T. A. H.

Brucine Polyhydrosulphides. ERNST SCHMIDT and D. BRUNS (Reprint from *Apoth. Zeit.*, 1911, No. 67).—Schmidt has shown already (this Journ., 1876, ii, 94) that when hydrogen sulphide is passed through a solution of brucine in alcohol, a yellow and a red polyhydrosulphide are formed, to which the formulæ $B_2,H_2S_6,2H_2O$ and $B_2,2H_2S_6$ were assigned respectively. Doebner subsequently prepared (Abstr., 1895, i, 403) by the addition of ammonium polysulphide to brucine in alcohol, an orange-red polyhydrosulphide, to which he assigned the formula $B_2,H_2S_8,2H_2O$. It is now shown that Doebner's compound is identical with Schmidt's red polyhydrosulphide.

T. A. H.

Dihydroterpenylamine. GEORGE FRANCIS MORRELL (*Ber.*, 1911, 44, 2560—2565).—When dihydrocarvylamine in dry ether is saturated with hydrogen chloride, at first at 0° and finally without cooling, an unstable *dihydrochloride*, $C_{10}H_{20}NCl,HCl$, white needles, m. p. 206°, is obtained. When this salt is heated with pyridine at 140—145°, it is converted into a *substance*, $C_{10}H_{19}N$, b. p. 96—100°/16 mm., D [illegible] 0·9[illegible], $n_D^{16\cdot6}$ 1·49284 (*picrate*, m. p. about 176°), which is found to be a mixture of two stereoisomerides, α- and β-dihydroterpenylamine. Methods for their separation are indicated. α-*Dihydroterpenylamine*, b. p. 96—97°/15 mm., forms a *benzoyl* derivative, m. p. 219°, a suspension of which in glacial acetic acid is converted, by treatment with 10—15% ozone and subsequent heating on the water-bath, into acetone and a ketonic *substance*, $C_{14}H_{17}O_2N$, m. p. 183—185°, which is stated to be 2-benzoylamino-1-methyl*cyclo*hexan-4-one.

β-*Dihydroterpenylamine*, b. p. 100—101°/16 mm., forms more sparingly soluble salts than the α-base; the *nitrate*, m. p. 179° (decomp.), *picrate*, m. p. 195°, *hydrochloride*, m. p. 235° (decomp.), and *benzoyl* derivative, m. p. 178—179°, are described.

When a suspension of benzoyldihydrocarvylamine in acetic acid is ozonised and the product heated on the water-bath, a ketonic *substance*, $C_{16}H_{21}O_2N$, m. p. 218—219°, is obtained, which is regarded as 2-benzoylamino-4-acetyl-1-methyl*cyclo*hexane. C. S.

Action of Carbon Tetrabromide on Organic Bases. WILLIAM M. DEHN and ALBERT H. DEWEY (*J. Amer. Chem. Soc.*, 1911, 33, 1588—1598).—Carbon tetrabromide unites with organic bases to form molecular compounds, the best results being obtained by mixing solutions of the substances in dry ether. In order to explain the mechanism of formation of these compounds, it is suggested that a "coalescence" first takes place, due to the residual valencies of the nitrogen and bromine, thus $\begin{array}{c}R\cdot NH_2\\ \| \\ Br\cdot CBr_3\end{array}$, and that this is followed by a shifting of the bonds, as shown by the formula $\begin{array}{c}R\cdot NH_2\\ \diagup \\ Br\ CBr_3\end{array}$. In the case of pyridine and piperidine, one molecule of the base unites with two molecules of carbon tetrabromide. It is evident that these two molecules are held with different degrees of tenacity, since vapour pressure curves indicate a dissociation of one molecule at 100°, and of the second molecule between 100° and 210°. Moreover, the complex compound is decomposed by water in accordance with the equation $C_5H_7N,2CBr_4 + 2H_2O \longrightarrow CBr_4 + CO_2 + 3HBr + C_5H_7N,HBr$. The pyridine compound therefore has the structure: $\begin{array}{l}C_5H_5N\cdot CBr_3\\ \quad\ \ | \\ \quad\ \ Br\vdots Br\cdot CBr_3\end{array}$.

$$\begin{array}{l}C_5H_5N\cdot CBr_3\\ \quad\ \ | \\ \ \ Br\cdot Br\cdot CBr_3\end{array}, \quad \text{or} \quad \begin{array}{l}C_5H_5N\cdot Br\\ \qquad\ | \\ \ \ Br_2C\cdot Br\vdots Br\cdot CBr_3\end{array} \longrightarrow \begin{array}{l}C_5H_5N\cdot Br\\ \qquad\ | \\ \ \ Br_2C\cdot Br\cdot CBr_3.\\ \qquad\ \ | \\ \qquad\ \ Br\end{array}$$

The *piperidine* compound, $C_5H_{11}N,2CBr_4$, m. p. 148°, crystallises in prismatic needles. The *pyridine* compound, $C_5H_5N,2CBr_4$, m. p. 218—220°, D^{21} 2·70, forms iridescent crystals, and is not decomposed

boiling alcohol. The *quinoline* compound, C_9H_7N,CBr_4, m. p. 47°, crystallises in white, prismatic needles. The 2-*picoline* compound, $C_6H_7N,2CBr_4$, m. p. 214°, forms large needles. With 2:6-lutidine, a product, m. p. 106°, was obtained in clusters of short needles; this may have been either the compound, $C_5H_3Me_2N,CBr_4$, or a mixture of the compound $C_5H_3Me_2N,2CBr_4$ with lutidine hydrobromide. Carbon tetrabromide reacts with phenylhydrazine with evolution of nitrogen and formation of bromoform and phenylhydrazine hydrobromide. On the addition of carbon tetrabromide to benzylamine, benzylamine hydrobromide separates. Diisoamylamine and dipropylamine yield products which are probably mixtures of the carbon tetrabromide compound with the hydrobromide of the base. With ethylamine, ethylamine *hydrobromide*, m. p. 157°, and the *compound*, $4NH_2Et,CBr_4$, m. p. 150°, are produced.

The following salts were obtained during the course of this work. Piperidine *auribromide*, m. p. 242°; pyridine *auribromide*, m. p. 319°; quinoline *hydrobromide*, m. p. 62—65°, and *auribromide*, m. p. 209°; picoline *auribromide*, m. p. 209°; 2:6-lutidine *hydrobromide*, m. p. 114°, and *auribromide*, m. p. 180°; benzylamine *auribromide*, m. p. 175°; and ethylamine *auribromide*, m. p. 190°. E. G.

Homologous Nature of Anthranil and Methylanthranil. JOHANNES SCHEIBER (*Ber.*, 1911, 44, 2409—2418).—The question whether anthranil, $C_6H_4<{CO \atop NH}$ or $C_6H_4<{CH \atop N}>O$, and methylanthranil, $C_6H_4<{CMe \atop N}>O$, are homologous has very frequently been the subject of discussion. It is shown by measurement of the ultra-violet absorption that the two compounds behave absolutely identically, and are therefore homologous.

Heller (Abstr., 1908, i, 267; 1909, i, 832) has shown that anthranil and methylanthranil behave differently towards 23% hydrochloric acid and sodium nitrite, but that they behave similarly when 39% acid is used. Measurements of the ultra-violet absorption of the two compounds in acids of these strengths show them to be identical in 4·9% acid, to differ in 24·5% acid, and to be identical again in 39% acid. Anthranil is shown to be very stable towards hydrogen chloride, and the change in absorption is not due to an opening of the ring. When kept for twelve days in 4·9% acid solution, anthranil gives slightly different curves; those for methylanthranil correspond with the readings taken immediately on dissolution.

Anthroxanic acid, $C_6H_4<{C(CO_2H) \atop N}>O$, likewise shows the same ultra-violet absorption as the two anthranils. The absorption in this case is not altered by solution in hydrochloric acid; possibly the alteration in the case of the homologous anthranils is due to salt formation. E. F. A.

Constitution of the ψ-Bases of Quinoline. II. ADOLF KAUFMANN and J. M. PLÁ Y JANINI (*Ber.*, 1911, 44, 2670—2677).—Kaufmann and Strübin (this vol., i, 321) have recently obtained

experimental evidence in support of the view that the pseudo-bases (quinolanols) of the quinoline series slowly undergo transformation into the isomeric *o*-alkylaminocinnamaldehydes, owing to the rupture of the pyridine ring. According to this view, 2-substituted quinoline bases should give rise to derivatives of cinnamic acid. The present paper contains an account of the reactions of 2-hydroxy-2-phenyl-1-methylquinoline (I) and its transformation into phenyl *o*-methylaminostyryl ketone (II):

$$C_6H_4{<}^{CH=CH}_{NMe\cdot CPh\cdot OH} \quad \longrightarrow \quad C_6H_4{<}^{CH:CH\cdot COPh}_{NHMe}$$

(I.) (II.)

2-Phenylquinoline methiodide (Doebner and Miller, Abstr., 1896, 721) is best prepared by the action of magnesium phenyl bromide on quinoline methiodide and subsequent oxidation of the resulting 2-phenyl-1-methyl-1 : 2-dihydroquinoline (compare Freund, Abstr., 1905, i, 156) with alcoholic iodine; its solution in water is colourless, in alcohol yellow, and in chloroform orange-red. When treated with aqueous sodium hydroxide, it yields the corresponding ψ-base (Decker and Fellenberg, Abstr., 1907, i, 1064), which is converted by the action of aqueous hydrochloric acid on its benzene solution into 2-*phenylquinoline methochloride*. This crystallises in long, almost colourless needles, which begin to decompose at 170°, and melt at 195—200° to a clear liquid; it is identical with the compound obtained by the interaction of silver chloride and 2-phenylquinoline methiodide. When treated with aniline and potassium hydroxide, the methiodide yields *phenyl* o-*methylaminostyryl ketoneanil*,

$$NHMe\cdot C_6H_4\cdot CH:CH\cdot CPh:NPh,$$

which crystallises in greenish-yellow needles, melting at 140° to a green liquid. The anil is unstable, and readily decomposes when heated alone or in benzene solution, yielding a green dye. It is hydrolysed by cold mineral acids into its components; thus, with hydrochloric acid, it yields aniline and 2-phenylquinoline methochloride.

An alkaline suspension of the above-mentioned ψ-base is oxidised by exposure to air, or more rapidly by potassium ferricyanide, to *ω-benzoyl-*o*-methylaminoacetophenone* (III), which crystallises from benzene in stout needles, m. p. 123°. The latter compound dissolves in acids, yielding salts of 4-keto-2-phenyl-1-methyl-3 : 4-dihydroquinolium hydroxide (IV); the *chloride*, $C_{16}H_4ONCl$, crystallises in stellar aggregates of almost colourless needles, m. p. 237° (decomp.), the *iodide* is light yellow, m. p. 220°; the *picrate*, $C_{22}H_{16}O_8N_4$, forms yellow crystals, m. p. 180°. The salts are reconverted by the action of sodium carbonate or ammonia, or even by boiling with water, into ω-benzoyl-*o*-methylaminoacetophenone, as represented in the following scheme:

$$C_6H_4{<}^{CO\cdot CH_2\cdot COPh}_{NHMe} \quad \underset{\text{Alkali}}{\overset{\text{HCl}}{\rightleftarrows}} \quad C_6H_4{<}^{CO——CH_2}_{NMeCl:CPh}$$

(III.) (IV.)

When heated at 250—260°, the chloride loses methyl chloride, yielding 4-hydroxy-2-phenylquinoline, m. p. 256° (Conrad and Limpach, Abstr.,

1888, 505), which is transformed by distillation with zinc dust into 2-phenylquinoline, and by the action of phosphorus pentachloride into 4-chloro-2-phenylquinoline (Knorr and Fertig, Abstr., 1897, i, 371). An explanation is also given of the oxidation of 4-cyano-1-alkyl-dihydroquinolines to 4-cyano-1-alkyl-2-quinolones, observed by Kaufmann and Albertini (Abstr., 1909, i, 958). It is assumed that the hydrogen in the 4-position is first oxidised to hydroxyl with the formation of the compound (V), which then undergoes transformation into (VI) by the addition of water and simultaneous rupture of the pyridine ring:

$$\underset{\text{(V.)}}{C_6H_4\left\langle\begin{array}{l}C(CN)(OH)\cdot CH\\ NR\text{————}CH\end{array}\right.} \longrightarrow \underset{\text{(VI.)}}{C_6H_4\left\langle\begin{array}{l}C(CN)(OH)\cdot CH_2\cdot CHO\\ NHR\end{array}\right.};$$

4-cyano-1-alkyl-2-quinolones are formed from this intermediate product by oxidation and loss of two molecules of water. The above-mentioned formation of ω-benzoyl-*o*-methylaminoacetophenone may be explained in a similar manner. F. B.

Condensation Products of Isatic Acid and Hydroxythionaphthen, Indandione, and Indanone. Emilio Noelting and Alex. Herzbaum (*Ber.*, 1911, **44**, 2585—2590).—Isatin in alkaline solution reacts with hydroxythionaphthen, indandione, or indanone just as with indoxyl (Noelting and Steuer, this vol., i, 165), yielding the following substances in accordance with the scheme:

$$C_6H_4\left\langle\begin{array}{l}CO\\ X\end{array}\right\rangle CH_2 + NH_2\cdot C_6H_4\cdot CO\cdot CO_2H \longrightarrow$$

$$C_6H_4\left\langle\begin{array}{l}N\text{=====}C\text{—}\\ C(CO_2H):C\cdot X\end{array}\right\rangle C_6H_4,$$

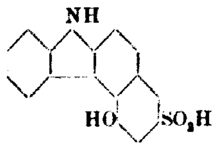
where $X = S$, CO, or CH_2. Thus hydroxythionaphthen yields "*thioquindolinecarboxylic acid*," $C_{16}H_9O_2NS$, yellow needles, which decomposes above its m. p., about 335°, forming "thioquindoline," m. p. 172° (not 169°, *loc. cit.*). Indandione yields *quinolylenephenyleneketonecarboxylic acid*, $C_{17}H_9O_3N$, colourless needles, which is converted into the corresponding ketone (Noelting and Blum, Abstr., 1901, i, 728) above its m. p., about 340°. Indanone yields *quinolylenephenylenemethanecarboxylic acid*, $C_{17}H_{11}O_2N$, m. p. 330° (decomp), which is converted by fusion into quinolylenephenylenemethane (Noelting and Blum, *loc. cit.*); the latter has also been obtained by condensing indanone and *o*-aminobenzaldehyde in boiling dilute hydrochloric acid.

The sodium salts of the three preceding acids yield with metallic salts precipitates, the colours of which are tabulated. C. S.

[Preparation of Carbazole Derivatives.] Kalle & Co. (D.R.-P. 234338).—Carbazole derivatives obtained from 6-amino-1-naphthol-3-sulphonic acid and hydrazines have previously been described, and the reaction has now been extended to the case of 7-amino-1-naphthol-3-sulphonic acid.

The carbazole, 1-*hydroxybenzo-β-naphthindole-3-sulphonic acid*

(annexed formula), is prepared by heating this acid in aqueous solution with phenylhydrazine in the presence of sodium hydrogen sulphite and sodium hydroxide; on cooling, the carbazole separates in micro-crystalline form.



The action is stated to be widely applicable, both with regard to the acid and hydrazine or other aromatic base employed.

The dyes obtained from tetrazotised benzidine, coupled with the foregoing carbazole (1 mol.) and salicylic acid and resorcinol respectively, are described in the original. F. M. G. M.

Action of Hydroxylamine on Ketones of the Type R·CH:CH·CH:CH·COPh. ROBERTO CIUSA and A. TERNI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 25—30. Compare Abstr., 1908, i, 762; Ciusa and Bernardi, Abstr., 1910, i, 684).—The present paper is concerned with the further examination of α-cinnamylideneacetophenonehydroxylamineoxime, previously described.

Benzylidene-α-cinnamylideneacetophenonehydroxylamineoxime,

$$C_{24}H_{22}O_2N_2,$$

is obtained by boiling for one hour alcoholic solutions of benzaldehyde and the hydroxylamineoxime; it has m. p. 175°.

α-Cinnamylideneacetophenonehydroxylamineoxime, when oxidised with permanganate, yields benzoic acid and a 3-*phenyl*-5-*styryliso-oxazole*, $CHPh:CH\cdot\overset{CH\cdot CPh}{\overset{\|}{C}\text{——}O}{>}N$, which forms lustrous scales, m. p. 138°. The hydroxylamineoxime yields with nitrous acid (sodium nitrite and glacial acetic acid in the cold) an isomeride of α-cinnamylideneacetophenoneoxime, m. p. 124°, identical with the substance previously obtained among the secondary products of the reaction between cinnamylideneacetophenone and hydroxylamine (compare Ciusa and Terni, *loc. cit.*). To this substance the constitution of a 3-*phenyl*-5-*styryldihydro*isooxazole, $CHPh:CH\cdot\overset{CH_2\cdot CPh}{\overset{|}{CH}\text{——}O}{>}N$, is ascribed. It yields a *dibromo*-derivative, $C_{17}H_{15}ONBr_2$, which crystallises in small, colourless needles, m. p. 145°. When α-cinnamylideneacetophenonehydroxylamineoxime is boiled with 90% acetic acid or normal hydrochloric acid, it gives the α-oxime of m. p. 135°. This explains the fact that when hydroxylamine hydrochloride reacts with unsaturated ketones in the absence of sodium acetate only oximes, and not hydroxylamineoximes, are obtained (compare Ciusa and Bernardi, *loc. cit.*). R. V. S.

Aromatic ψ-Thiocarbamides and their Conversion into Aryl *ortho*-Thiocarbonates. FRITZ ARNDT (*Annalen*, 1911, **384**, 322—351). —The interaction of *p*-tolyl mercaptan and cyanamide, with the addition of ether to moderate the violence of the reaction, gives an almost quantitative yield of p-*tolyl*-ψ-*thiocarbamide*,

$$NH:C(NH_2)\cdot S\cdot C_7H_7,$$

m. p. 110° (decomp.). The substance decomposes when heated alone

or in boiling alcohol, yielding *p*-tolyl mercaptan and dicyanodiamide. It forms a *dibenzoate*, NBz:C(NHBz)·S·C_7H_7, m. p. 122—123°, with benzoyl chloride in cold pyridine, and also yields well crystallised salts, of which the *acetate*, *sulphate*, *chromate*, *chloride*, and *nitrate*, m. p. 173°, are described. Very characteristic is its behaviour in the presence of nitric and sulphuric acids, whereby a *nitrate-sulphate*,

$$3C_8H_{10}N_2S,H_2SO_4,HNO_3,$$

is obtained, even when the dilution of the nitric acid is one in 100,000; provided an excess of the reagent is present, this salt is so insoluble that it can be employed for the estimation of nitrates. Similar, sparingly soluble double salts are obtained in the presence of sulphuric acid and the majority of the monobasic acids or hydrosulphuric acid, but not hydroferricyanic acid, hydrogen cyanide, ferrocyanic acid, phosphoric acid, or organic acids; however, the place of the sulphuric acid cannot be taken by any other acid. (The isomeric benzyl-ψ-thiocarbamide does not form double salts corresponding with the preceding.)

p-Tolyl-ψ-thiocarbamide chloride or acetate reacts with concentrated sodium nitrate (not potassium nitrite) in neutral solution to form the *nitrite*, m. p. 112°, but in the presence of hydrochloric acid, *nitroso*-p-*tolyl-ψ-thiocarbamide*, $C_8H_9ON_3S$, decomp. 112°, is obtained, which receives the constitution $C_7H_7S·C(:NH)·NH·NO$ or

$$C_7H_7S·C(:NH)·N:N·OH$$

on account of its absence of colour, insolubility in dilute acids, response to the Liebermann test, and conversion by glacial acetic acid into nitrogen and *p*-tolyl thiocyanate. When the nitroso-compound is recrystallised from methyl alcohol without the addition of a little ammonia, it is partly converted into a yellow *substance*, decomp. about 130°, which is probably $C_7H_7S·CO·NH·NO$.

When its methyl-alcoholic solution is warmed with aqueous ammonia, nitroso-*p*-tolyl-ψ-thiocarbamide is converted into p-*tolyl orthothiocarbonate*, $C(S·C_7H_7)_4$, needles, m. p. 147°, which forms with bromine in chloroform an unstable *perbromide*, $C(S·C_7H_7)_4,Br_8$, dark red leaflets, m. p. below 100° (of freshly prepared specimen), which readily changes to a yellow, crystalline *tetrabromide*, $C(S·C_7H_7)_4,Br_4$, m. p. 169°. By boiling the tetrabromide with alcohol or warming the thiocarbonate itself with acetic and a little concentrated sulphuric acid, the *disulphoxide*, $C(S·C_7H_7)_2(SO·C_7H_7)_2$, m. p. 92°, is obtained. An attempt to synthesise *p*-tolyl orthothiocarbonate from sodium *p*-tolylmercaptide and carbon tetrachloride in boiling alcohol resulted in the formation of p-*tolyl orthothioformate*, $CH(S·C_7H_7)_3$, m. p. 111°, which is also produced by the reduction of the orthothiocarbonate by zinc and acetic acid.

Benzyl-ψ-thiocarbamide and sodium nitrite react in acid solution to form a stable *nitrite*, m. p. 126° (decomp.), which yields benzyl disulphide by heating; a substance corresponding with nitroso-*p*-tolyl-ψ-thiocarbamide is not formed.

p-Tolyl mercaptan and phenylcyanamide react in ether to form *phenyl*-p-*tolyl-ψ-thiocarbamide*, $NHPh·C(NH)·S·C_7H_7$, m. p. 148°, which forms a *hydrochloride*, *nitrate*, m. p. 132°, and *benzoyl* derivative, m. p. 151·5°, and is easily methylated, yielding *phenyl*-p-*tolylmethyl-ψ-thiocarbamide*, $NPhMe·C(NH)·S·C_7H_7$, m. p. 121°.

Diphenyl-p-tolyl-ψ-thiocarbamide, $NHPh\cdot C(NPh)\cdot S\cdot C_7H_7$, m. p. 119—120°, is obtained by desulphurising diphenylthiocarbamide in benzene by mercuric oxide and treating the resulting solution of carbodiphenylimide with *p*-tolyl mercaptan.

Hofmann's triphenyl*iso*melamine, m. p. 185° (Abstr., 1886, 139), is shown to be an additive compound of triphenylmelamine and phenylcyanamide; the former constituent can be removed by dilute acid or boiling water.

C. S.

Conversion of Nitroaldehydes into Cyanoaldehydes. GIACOMO PONZIO (*Gazzetta*, 1911, **41**, i, 787—793. Compare Ponzio and Giovetti, Abstr., 1910, i, 194).—The author has shown previously that an aliphatic nitro-group may be substituted by $-NH_2$ or $-NHPh$ (compare Abstr., 1910, i, 339, 442, 699), and he now finds that it may also be replaced by $-CN$. A new method of preparation is thus provided for the hydrazones of ω-cyanobenzaldehyde, which, although longer than that formerly given, has the advantage that the *o*- and *m*-substituted phenylhydrazones can also be obtained.

ω-Cyanobenzaldehyde-*o*-nitrophenylhydrazone (*loc. cit.*) is the only substance produced when ω-nitrobenzaldehyde-*o*-nitrophenylhydrazone is boiled for two hours in aqueous alcoholic solution with potassium cyanide.

ω-Cyanobenzaldehyde-m-*nitrophenylhydrazone*,

$$CN\cdot CPh\colon N\cdot NH\cdot C_6H_4\cdot NO_2,$$

which cannot be obtained by the method formerly given, crystallises in small, yellow prisms, m. p. 197—198°. It is soluble in alkali to which a drop of alcohol has been added, and it gives a yellow coloration. The *ω-nitrobenzaldehyde*-m-*nitrophenylhydrazone* employed for its preparation is obtained by heating the sodium salt of ω-nitrotoluene with *m*-nitrobenzenediazonium sulphate; it crystallises in small brick-red prisms, m. p. 132° (decomp.).

ω-Cyanobenzaldehyde-*p*-nitrophenylhydrazone, ω-cyanobenzaldehyde-*o*-chloro-*p*-nitrophenylhydrazone, and ω-cyanobenzaldehyde-*o*-*p*-dinitrophenylhydrazone can also be prepared by the new method. The *ω-nitrobenzaldehyde*-o-p-*dinitrophenylhydrazone* necessary for the preparation of the last-named substance is obtained by diazotising 2:4-dinitroaniline and acting on the sodium salt of ω-nitrotoluene with the 2:4-dinitrobenzenediazonium sulphate so produced. The substance crystallises in yellowish-brown, flat needles, m. p. 152° (decomp.).

R. V. S.

Syntheses of Pyrazolones from a Derivative of γ-Pyrone. F. CARLO PALAZZO and RAFFAELE LIVERANI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 55—60. Compare Palazzo, Abstr., 1906, i, 701).—By the action of hydrazine hydrate on ethyl dimethylpyronedicarboxylate the authors have obtained three different nitrogenous compounds, which all belong to the pyrazolone group. When 1 mol. of hydrazine hydrate is boiled with the ester in methyl-alcoholic solution for two minutes, a small quantity (2%) of a compound is obtained, which crystallises in minute needles, m. p. 195—196°, and gives a reddish-violet coloration with ferric chloride. Of this substance

no analysis could be made, but it is identical with the product $C_7H_{10}O_3N_2$, from hydrazine hydrate and ethyl acetylmalonate, which is known to be *3-methyl-5-pyrazolone-4-carboxylate*. When two mol. of hydrazine hydrate are heated in a sealed tube with a concentrated methyl-alcoholic solution of ethyl dimethylpyronedicarboxylate for some hours at 120°, a *substance*, $C_5H_5O_2N_2\cdot OEt$, is obtained in good yield. The compound has m. p. 125—130° (softening considerably at 50—60°), and gives a reddish-brown coloration with ferric chloride. It is suggested that it may be an isomeride of the first-mentioned compound. By the interaction of two mols. of hydrazine hydrate and ethyl dimethylpyronedicarboxylate in methyl-alcoholic solution as before, the mixture being boiled for two hours, a *substance* is produced, which has m. p. 142—145°. It gives a reddish-brown coloration with ferric chloride. The analytical results agree with the formula $C_{11}H_{16}O_4N_4$, but the substance appears to be a mixture, possibly of equimolecular amounts of the two pyrazolones, $C_7H_{10}O_3N_2$ and $C_4H_6ON_2$.

R. V. S.

The Pyrazoline Transformation of Unsaturated Hydrazones.

HUGO BAUER and HEDWIG DIETERLE (*Ber.*, 1911, 44, 2697—2702).—It has been shown by Auwers (Abstr., 1909, i, 59; 1910, i, 70) that the phenylhydrazones of many unsaturated ketones may be transformed into pyrazoline derivatives by heating them with glacial acetic acid. That the reaction is, however, not a general one has been confirmed by the authors from an examination of the behaviour of unsaturated ketones of the type $CHPh{:}CH\cdot CH{:}CH\cdot CO\cdot CH{:}CHR$. When R = anisyl or furyl, the action of phenylhydrazine leads directly to the formation of a pyrazoline derivative; the intermediately formed phenylhydrazones could not be isolated. On the other hand, when R = phenyl, the phenylhydrazone is not converted into a pyrazoline derivative, even by prolonged heating with acetic acid.

1-*Phenyl-3-β-styrylvinyl-5-anisylpyrazoline*,

$$CHPh{:}CH\cdot CH{:}CH\cdot C{<}{\genfrac{}{}{0pt}{}{-CH_2-}{N\cdot NPh}}{>}CH\cdot C_6H_4\cdot OMe,$$

prepared by heating anisylidenecinnamylideneacetone [*p*-methoxystyryl β-styrylvinyl ketone] with phenylhydrazine in glacial acetic acid solution, forms yellow crystals, m. p. 155—156°; its alcoholic solution has an intense, green fluorescence. When oxidised with aqueous potassium permanganate, it yields benzoic acid and 1-*phenyl-5-anisyl-pyrazole-3-carboxylic acid*, $OMe\cdot C_6H_4\cdot C{<}{\genfrac{}{}{0pt}{}{CH\text{——}}{NPh\cdot N}}{>}C\cdot CO_2H$, which crystallises from water in white needles, m. p. 178—179°, and yields a *copper* salt, $(C_{17}H_{15}O_3N_2)_2Cu$, crystallising in slender, green needles. The formation of this acid proves that the double linking, adjacent to the anisyl group, is concerned in the pyrazoline formation, and this is confirmed by the behaviour of the two following phenylhydrazones, which do not contain a double linking in this position, and, therefore, are not transformed into pyrazoline derivatives.

ζ-Bromo-η-methoxy-α-phenyl-η-anisyl-Δ^{αγ}-heptadien-ε-onephenylhydrazone, $CHPh{:}CH\cdot CH{:}CH\cdot C(N\cdot NHPh)\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe$,

obtained from the corresponding ketone (this vol., i, 881) and phenylhydrazine, has m. p. 201—202·5°.

γδζ-Tribromo-η-methoxy-α-phenyl-η-anisyl-Δ^α-hepten-ε-onephenylhydrazone, $CHPh\colon CH\cdot[CHBr]_2\cdot C(N\cdot NHPh)\cdot CHBr\cdot CH(OMe)\cdot C_6H_4\cdot OMe$, also prepared from the corresponding ketone (*loc. cit.*), forms slender, yellow needles, m. p. 181—182°.

Styryl β-styrylvinyl ketonephenylhydrazone,

$$CHPh\colon CH\cdot CH\colon CH\cdot C(\colon N\cdot NHPh)\cdot CH\colon CHPh,$$

prepared from its components in alcoholic solution, crystallises in yellowish-brown platelets, m. p. 111—112°.

Furfurylidenecinnamylideneacetone [*β-styryl-β′-furyldivinyl ketone*],

$$CHPh\colon CH\cdot CH\colon CH\cdot CO\cdot CH\colon CH\cdot C_4H_3O,$$

obtained by the condensation of furfuraldehyde with cinnamylideneacetone (β-styrylvinyl methyl ketone) by means of sodium hydroxide in aqueous alcoholic solution, crystallises in lustrous, golden-yellow leaflets, m. p. 97—98°. It gives an intense red coloration with strong nitric acid, and is transformed by the action of phenylhydrazine into 1-*phenyl*-3-*β-styrylvinyl*-5-*furylpyrazoline*,

$$CHPh\colon CH\cdot CH\colon CH\cdot C{\lesssim}{}^{CH_2}_{N\cdot NPh}{>}CH\cdot C_4H_3O,$$

which crystallises in strongly fluorescent, slender, yellow needles, m. p. 165—166°, and is oxidised by aqueous permanganate to benzoic acid and 1-*phenylpyrazole*-3 : 4-*dicarboxylic acid*, m. p. 250—255°.

F. B.

Hydantoins. IV. 2-Thio-1-phenylhydantoins from Some α-Amino-acids. CHARLES A. BRAUTLECHT (*J. Biol. Chem.*, 1911, **10**, 139—146. Compare Wheeler and Brautlecht, this vol., i, 509).—The action of phenylthiocarbimide on a number of α-amino-acids has been studied. In the presence of alkali, interaction takes place with the formation of alkali salts of thiohydantoic acids. These readily undergo transformation into the corresponding hydantoins on treatment with hydrochloric acid. Crystalline thiophenylhydantoins could not, however, be obtained from cystine and α-pyrrolidonecarboxylic acid.

These thiophenylhydantoins are characteristic of the α-amino-acids, and should serve for their identification. When warmed with potassium hydroxide, they are hydrolysed to the potassium salts of the thiohydantoic acids. They are desulphurised by digestion in aqueous or dilute alcoholic solutions with silver nitrate, mercuric chloride, etc., and are stable in the presence of boiling hydrochloric acid.

2-Thio-1-phenylhydantoin, $CS{<}{}^{NPh\cdot CO}_{NH-CH_2}$, from glycine has m. p. 240—242°.

2-*Thio*-1-*phenyl*-4-*ethylhydantoin* from α-amino-*n*-butyric acid crystallises in plates, m. p. 190—192°.

2-*Thio*-1-*phenyl*-4-*isopropylhydantoin*, obtained from valine, forms colourless needles, m. p. 206—208°.

2-*Thio*-1-*phenyl*-4-*benzylhydantoin* from phenylalanine separates in colourless prisms, m. p. 187°.

Tyrosine gives rise to 2-*thio*-1-*phenyl*-4-p-*hydroxybenzylhydantoin*, colourless or straw-coloured prisms, m. p. 214—216°.

From asparagine 2-*thio*-1-*phenylhydantoin*-4-*acetamide* is obtained; it crystallises in colourless, lenticular prisms, m. p. 234°.

The *potassium* salt of the hydantoic acid,

$$NHPh\cdot CS\cdot NH\cdot CH(CO_2K)\cdot CH_2\cdot CO\cdot NH_2,$$

separates in colourless plates, m. p. 154°.

2-*Thio*-1-*phenylhydantoin*-4-*acetic acid*, $\begin{matrix}NPh\cdot CO\\ CS-NH\end{matrix}\!\!>\!CH\cdot CH_2\cdot CO_2H$, from aspartic acid crystallises in colourless prisms, m. p. 233—234° (decomp.).

2-*Thio*-1-*phenylhydantoin*-4-*propionic acid*, prepared from glutamic acid, separates in microscopic needles, m. p. 169—170°. E. F. A.

Hydantoins. V. Synthesis of 3 : 5-Dichlorotyrosine. Henry L. Wheeler, Charles Hoffman, and Treat B. Johnson (*J. Biol. Chem.*, 1911, 10, 147—157).—Tyrosine itself does not react smoothly with chlorine, but tyrosinehydantoin reacts with chlorine in glacial acetic acid solution, forming the corresponding *hydantoin* of 3 : 5-*dichlorotyrosine*. The same compound was obtained on reducing 3 : 5-dichlorobenzylidenehydantoin with hydriodic acid, a compound which was prepared by Wheeler and Hoffmann (this vol., i, 498) by condensation of hydantoin with 3 : 5-dichlorobenzaldehyde. Chlorine therefore is substituted in the same positions (3 : 5) in the benzene nucleus of tyrosinehydantoin as are taken by iodine and bromine when they combine with tyrosine. On digestion with barium hydroxide, the hydantoin is converted into 3 : 5-*dichlorotyrosine*. This crystallises with $2H_2O$, dissociates in aqueous solution, and reacts acid to litmus; it does not give a red coloration with Millon's reagent.

Benzylidenehydantoin reacts with chlorine and bromine in acetic acid, forming α-*chloro*- and α-*bromo-benzylidenehydantoin* respectively. The latter is reduced by hydriodic acid, forming benzylhydantoin. Anisylidenehydantoin was not reduced under practically the same conditions.

3 : 5-*Dichlorotyrosinehydantoin* crystallises in rhombohedral prisms, m. p. 202° (decomp.).

3 : 5-*Dichlorotyrosine* separates in rectangular, prismatic crystals, m. p. 252° (decomp.). The *hydrochloride* forms large, prismatic, colourless crystals, m. p. 260—265° (decomp.).

α-*Bromobenzylidenehydantoin*, $\begin{matrix}NH\cdot CO\\ CO\cdot NH\end{matrix}\!\!>\!C:CBrPh$, crystallises in plates, m. p. 240° to an oil.

α-*Thiolbenzylidenehydantoin*, prepared by boiling the bromo-compound with potassium hydrosulphide, crystallises in yellow prisms, m. p. 199° (decomp.).

α-*Chlorobenzylidenehydantoin* also crystallises in plates, m. p. 273° to an oil.

p-*Methoxybenzylhydantoin*, prepared by reduction of anisylidenehydantoin (Wheeler and Hoffman, *loc. cit.*), crystallises in yellow, hexagonal tablets, m. p. 174° to a clear oil. Anisylidenehydantoin could not be reduced with tin and hydrochloric acid; after boiling

with zinc and acetic acid, it was recovered unchanged, but in a colourless form. Digestion with sodium hydroxide converts it into *p*-methoxyphenylpyruvic acid. E. F. A.

Pyrimidines. LIII. Condensation of Ethyl Formate and Ethyl Oxalate with Some Pyrimidinethioglycollates. TREAT B. JOHNSON and NORMAN A. SHEPARD (*Amer. Chem. J.*, 1911, 46, 345—361).—The work described was undertaken with the object of obtaining further knowledge of the behaviour of the grouping $-S\cdot CH_2\cdot CO-$. Johnson and Guest (Abstr., 1909, i, 744) have studied the condensation of ethyl formate with ethyl benzylthiolacetate, and Hinsberg (Abstr., 1910, i, 334) has shown that the methylene group in ethyl thiodiglycollate react readily with α-dicarbonyl compounds.

The only pyrimidine derivative of ethyl thiolacetate hitherto described is ethyl 1 : 6-dihydro-6-pyrimidone-2-thiolacetate, which was obtained by Wheeler and Liddle (Abstr., 1909, i, 61) by the action of ethyl chloroacetate on 2-thiouracil. It is now shown that *trans-β-thiocarbaminoacrylic acid*, $NH_2\cdot CS\cdot NH\cdot CH{:}CH\cdot CO_2H$, which forms lustrous plates and does not melt below 300°, is also produced in this reaction.

Ethyl 1 : 6-dihydro-6-pyrimidone-2-thiolacetate condenses with ethyl formate in presence of sodium ethoxide with formation of *ethyl 1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate*,

$$NH<\begin{matrix}C[S\cdot C(CH\cdot OH)\cdot CO_2Et]{:}N\\ CO\text{———————}CH\end{matrix}>CH,$$

m. p. 138—140°, which crystallises in prisms.

By the condensation of ethyl oxalate with 1 : 6-dihydro-6-pyrimidone-2-thiolacetate, *diethyl 1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate*, $NH<\begin{matrix}C[S\cdot CH(CO\cdot CO_2Et)\cdot CO_2Et]{:}N\\ CO\text{————————}CH\end{matrix}>CH$, m. p. 171°, is obtained, which crystallises in stout blocks, and is decomposed by hydrochloric acid with formation of *1 : 6-dihydro-6-pyrimidone-2-thiolpyruvic acid*, $NH<\begin{matrix}C(S\cdot CH_2\cdot CO\cdot CO_2H){:}N\\ CO\text{—————}CH\end{matrix}>CH$, m. p. 200—201° (decomp.); it is also decomposed by potassium hydroxide with production of uracil.

When ethyl 1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate is heated with thiocarbamide in presence of sodium ethoxide, *2-(tetrahydro-2'-thio-6'-pyrimidonethiol)-1 : 6-dihydro-6-pyrimidone*,

$$CS<\begin{matrix}NH-CO\\ NH\cdot CH\end{matrix}>C\cdot SC<\begin{matrix}NH\cdot CO\\ N-CH\end{matrix}>CH,$$

is produced, which crystallises in needles and decomposes at 285—295°. Thiocarbamide also condenses with ethyl 1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate with formation of small quantities of a compound which is probably identical with that just described.

Ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate,

$$NH<\begin{matrix}C(S\cdot CH_2\cdot CO_2Et){:}N\\ CO\text{—————}CH\end{matrix}>CMe,$$

m. p. 145—146°, obtained by the action of ethyl chloroacetate on 2-thio-4-methyluracil, forms colourless needles; the corresponding acid, m. p. 192—197° (decomp.), crystallises in colourless prisms; the *potassium* salt is described.

When ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate is heated with ethyl formate in presence of sodium ethoxide, *ethyl methyl-1 : 6-dihydro-6-pyrimidone-2-α-thiol-β-hydroxyacrylate*,

$$\mathrm{NH}{<}\begin{matrix}\mathrm{C[S\cdot C(CH\cdot OH)\cdot CO_2Et]:N}\\ \mathrm{CO\text{————————}CH}\end{matrix}{>}\mathrm{CMe},$$

m. p. 106—108°, is produced, which forms colourless crystals; an attempt to reduce this compound with sodium amalgam resulted in the formation of 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetic acid. By the condensation of thiocarbamide with ethyl 4-methyl-1 : 6-dihydro-pyrimidone-2-α-thiol-β-hydroxyacrylate, *4-methyl-2(tetrahydro-2′-thio-pyrimidonethiol)-1 : 6-dihydro-6-pyrimidone*,

$$\mathrm{CS}{<}\begin{matrix}\mathrm{NH-CO}\\ \mathrm{NH\cdot CH}\end{matrix}{>}\mathrm{C\cdot SC}{<}\begin{matrix}\mathrm{NH\cdot CO}\\ \mathrm{N-CMe}\end{matrix}{>}\mathrm{CH},$$

is produced, which forms clusters of prisms, and does not melt below 300°.

Diethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thioloxalylacetate,

$$\mathrm{NH}{<}\begin{matrix}\mathrm{C[S\cdot CH(CO\cdot CO_2Et)\cdot CO_2Et]:N}\\ \mathrm{CO\text{————————}CH}\end{matrix}{>}\mathrm{CMe},$$

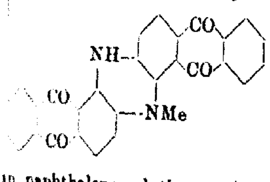
m. p. 139—140°, obtained by the action of ethyl oxalate on ethyl 4-methyl-1 : 6-dihydro-6-pyrimidone-2-thiolacetate, crystallises in stout, colourless blocks; it condenses with thiocarbamide with formation of a *compound*,

$$\begin{matrix}\mathrm{NH\cdot CO\cdot C-S-C{=}N-CO}\\ \mathrm{CS\cdot NH\cdot C\cdot CO\cdot N\cdot CMe:CH}\end{matrix} \quad\text{or}\quad \begin{matrix}\mathrm{NH\cdot CO\cdot C-S-C{=}N-CMe}\\ \mathrm{CS\cdot NH\cdot C\cdot CO\cdot N\cdot CO\cdot CH}\end{matrix},$$

m. p. 164—165°, which crystallises in hexagonal tablets. E. G.

Preparation of Halogenated Derivatives of Indigotin. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 234961).—When 4 : 4′-dichloroindigotin is suspended in nitrobenzene (or other indifferent liquids), cooled, and treated with chlorine, further halogenation takes place, yielding tri- and tetra-chloro-derivatives. The corresponding bromo-derivatives are obtained when the substance is suspended in dilute sulphuric acid and treated with bromine at a temperature below 5°. F. M. G. M.

[Preparation of Methylindanthren.] FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234294). — *Methylindanthren* (annexed formula), dark blue needles with metallic lustre, is prepared by boiling 2-bromo-1-aminoanthraquinone with 2-bromo-1-methylaminoanthraquinone in the presence of sodium acetate and cupric chloride in naphthalene solution; it dissolves with a yellowish-brown colour in concentrated sulphuric acid. F. M. G. M.



Action of Nitrous Acid on Substituted Hydrazidines. GIACOMO PONZIO and C. GASTALDI (*Gazzetta*, 1911, 41, i, 793—796).—The substituted hydrazidines previously described (compare Ponzio, Abstr., 1910, i, 443, 699) when treated with nitrous acid do not yield

tetrazoles, but, instead, the hydrogen of the imino-group is displaced by –NO, so that ω-aminobenzaldehyde-p-nitrophenylhydrazone,

$$NH_2\cdot CPh:N\cdot NH\cdot C_6H_4\cdot NO_2,$$

yields *ω-aminobenzaldehydenitroso-p-nitrophenylhydrazone*,

$$NH_2\cdot CPh:N\cdot N(NO)\cdot C_6H_4\cdot NO_2.$$

This nitroso-compound is insoluble in alkali hydroxides, and when boiled with water gives ω-aminobenzaldehyde-p-nitrophenylhydrazone and benzoyl-p-nitrophenylhydrazine, $COPh\cdot NH\cdot NH\cdot C_6H_4\cdot NO_2$.

ω-Aminobenzaldehydenitroso-p-nitrophenylhydrazone forms small, yellow laminæ, m. p. 127° (decomp.). It gives an emerald-green coloration with concentrated sulphuric acid and phenol. R. V. S.

Preparation of Secondary 4-Dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone Citrate. RUDOLF OTTO (D.R.-P. 234631).—Two salts of this base with citric acid have previously been described, and the "citrovanille" employed in pharmacy consists of mixtures of both in varying proportions. The primary salt (a syrup) is prepared from equal molecular proportions of the base and acid, the tertiary, containing 3 mols. of the base, has similar properties, while the secondary, *4-dimethylamino-1-phenyl-2 : 3-dimethyl-5-pyrazolone citrate*, $C_6H_8O_7(C_{13}H_{17}ON_3)_2$, has now been prepared by allowing the requisite proportions of the components to react either in warm aqueous solution at 75° or in a fusion without solvent; it crystallises from hot water. F. M. G. M.

Isomeride of *apo*Safranine and the Third Isomeride of Phenosafranine. FRIEDRICH KEHRMANN and JOSÉ RIERA Y PUNTI (*Ber.*, 1911, 44, 2622—2627).—*2 : 4 : 6 : 5′-Tetranitro-2′-anilinodiphenylamine*, $C_6H_2(NO_2)_3\cdot NH\cdot C_6H_3(NO_2)\cdot NHPh$, brownish-yellow crystals, decomp. above 174°, obtained by warming equal molecular quantities of picryl chloride and 4-nitro-2-aminodiphenylamine in alcoholic solution, is converted in alcoholic suspension by concentrated sodium hydroxide into *1 : 3 : 7-trinitro-10-phenyldihydrophenazine*, $C_6H_2(NO_2)_2{<}{}^{NH}_{NPh}{>}C_6H_3\cdot NO_2$, blackish-violet needles, decomp. above 265°, which dissolves in hot alcoholic sodium hydroxide with a violet colour. When suspended in glacial acetic acid and reduced by stannous chloride and hydrochloric acid, it is reduced to the *triamino-phenyldihydrophenazine* (isolated as the yellow *stannichloride*), which loses ammonia by careful warming in faintly alcoholic solution, the subsequent addition of sodium chloride precipitating *2 : 6-diamino-10-phenylphenazonium chloride*, $NH_2\cdot C_6H_3{<}{}^{N}_{NPhCl}{>}C_6H_3\cdot NH_2$. This salt forms blackish-violet, prismatic crystals with a bronze lustre, yields a violet-blue aqueous solution (so also do other mono-acidic salts), a brown solution in slightly fuming sulphuric acid, and a greenish-blue solution in concentrated sulphuric acid, which changes to magenta-red and finally to violet-blue on sufficient dilution with water; these colour changes indicate the existence of four series of salts, as is the case with phenosafranine itself. This new *iso*-phenosafranine dyes tannined cotton a dirty greenish-blue, the

colour changing to red by treatment with dilute hydrochloric acid, and by washing to a blue which is fast to alkalis and soap.

*iso*Phenosafranine chloride and acetic anhydride at the ordinary temperature yield an *acetyl* derivative,

$$NH_2 \cdot C_6H_3 \lessdot \genfrac{}{}{0pt}{}{N\text{———}}{NPhCl} \gtrdot C_6H_3 \cdot NHAc,$$

reddish-brown needles, from which by the elimination of the amino-group is obtained the *acetyl* derivative of *iso-apo*safranine chloride, $C_6H_4 \lessdot \genfrac{}{}{0pt}{}{N\text{———}}{NPhCl} \gtrdot C_6H_3 \cdot NHAc$; the corresponding *nitrate*, *ferrichloride*, and *platinichloride* are mentioned. iso-apo*Safranine chloride*, obtained by hydrolysing the preceding acetyl derivative, is an almost black, crystalline powder, which is unstable in solution; the *platinichloride*, $2C_{18}H_{14}N_3, PtCl_6$, is a black, crystalline powder.

*iso*Phenosafranine chloride and acetic anhydride and sodium acetate on the water-bath yield the *diacetyl* derivative,

$$NHAc \cdot C_6H_3 \lessdot \genfrac{}{}{0pt}{}{N\text{———}}{NPhCl} \gtrdot C_6H_3 \cdot NHAc,$$

brownish-red crystals with a bronze lustre; the *platinichloride* is a brownish-red, crystalline substance. C. S.

Third Isomeride of *apo*Safranine. FRIEDRICH KEHRMANN and A. MASSLENIKOFF (*Ber.*, 1911, **44**, 2628—2631. Compare preceding abstract).—When the green *iso*phenosafranine chloride (1 : 3-diamino-10-phenylphenazonium chloride) undergoes prolonged treatment at the ordinary temperature with acetic anhydride and acetic acid, it is converted into *3-amino-1-acetylamino-10-phenylphenazonium chloride*, $NHAc \cdot C_6H_2(NH_2) \lessdot \genfrac{}{}{0pt}{}{N\text{———}}{NPhCl} \gtrdot C_6H_4$, bronze crystals (the *platinichloride*, *dichromate*, *aurichloride*, and *iodide* are described), from which *1-amino-10-phenylphenazonium* salts are obtained by elimination of the amino-group and subsequent hydrolysis; the *nitrate*, *bromide*, *platinichloride*, *dichromate*, *iodide*, and *aurichloride* are described. The *acetyl* derivative, which is prepared best from the bromide, is obtained in small, chocolate-brown crystals, and forms a dark brown, crystalline *platinichloride*. C. S.

Synthesis of Naphthaphenazine Derivatives. FRIEDRICH KEHRMANN and JOSÉ RIERA Y PUNTI (*Ber.*, 1911, **44**, 2618—2621).—*2 : 4-Diaminonaphthaphenazine*, $C_{10}H_6 \lessdot \genfrac{}{}{0pt}{}{N}{N} \gtrdot C_6H_2(NH_2)_2$, obtained by reducing picryl-β-naphthylamine with the calculated amount of stannous chloride in boiling alcohol and concentrated hydrochloric acid, is purified best by means of the *diacetyl* derivative, yellow leaflets, m. p. 340° (decomp.), and forms red crystals which sublime at 320° with partial decomposition. Its diacetyl derivative does not form an azonium compound with methyl sulphate.

1 : 3-Diaminonaphthaphenazine, obtained in a similar manner from picryl-α-naphthylamine, forms dark red crystals and sublimes at 290—300° (decomp.). The *diacetyl* derivative, yellow needles, m. p. 320° (decomp.), easily combines with methyl sulphate in nitrobenzene

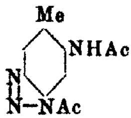
at 150°, yielding after hydrolysis with concentrated hydrochloric acid, 1 : 3-*diaminomethylnaphthaphenazonium chloride*,

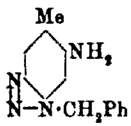
$$C_6H_2(NH_2)_2{<}\genfrac{}{}{0pt}{}{N\longrightarrow}{N(MeCl)}{>}C_{10}H_6,$$

dark red needles; the *platinichloride*, $2C_{17}H_{15}N_4,PtCl_6$, is described.

C. S.

Preparation of Iminoalkyl Derivatives of Azimino-toluidides. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 234966).—*Acetylaziminoaceto*-o-*toluidide* (annexed formula), m. p. 222—224°, was prepared by the reduction (iron and acetic acid) and subsequent diazotisation of 5-nitro-diacetyl-*m*-tolylenediamine; the acetyl group in the azimino-ring was then eliminated by boiling with sodium hydroxide, yielding on acidification 4 : 5-*azimino*-2-*aceto*-o-*toluidide*, a colourless powder, m. p. 235—237°; this was converted into its *benzyl* derivative, the remaining acetyl group removed by heating with sulphuric acid, and the resulting 4 : 5-*benzylazimino*-o-*toluidine* (annexed formula) precipitated with an alkali hydroxide; it forms a crystalline powder, m. p. 161—163°.





Other alkyl derivatives of this base can be readily prepared in a similar manner.

F. M. G. M.

Diguanides. GEORG COHN (*J. pr. Chem.*, 1911, [ii], **84**, 394—409).—Diguanides of the type $NH{:}C(NHR){\cdot}NH{\cdot}C(NH_2){:}NH$, where R = aryl, are readily obtained in the form of their hydrochlorides by heating dicyanodiamide with the hydrochlorides of aromatic amines in aqueous solution.

Phenyldiguanide (Lumière and Perrin, Abstr., 1905, i, 249), prepared from aniline hydrochloride and dicyanodiamide, forms a *picrate*, crystallising in yellow needles, m. p. 176—179°, with previous sintering.

m-*Nitrophenyldiguanide*, $NO_2{\cdot}C_6H_4{\cdot}C_2H_6N_5$, obtained from *m*-nitroaniline, forms amber-yellow prisms or rhombic leaflets, m. p. 147—149°; it crystallises with alcohol in transparent prisms having a colour resembling that of potassium dichromate; it forms a yellow *hydrochloride* and a *picrate*, m. p. 210—211°.

p-Hydroxyphenyldiguanide, $OH{\cdot}C_6H_4{\cdot}C_2H_6N_5$, prepared from *p*-aminophenol hydrochloride, crystallises in spherical aggregates of long, white needles, which become brown at 200° and have m. p. 211°; the hydrochloride has m. p. 203° (compare *loc. cit.*); the *picrate*, m. p. 205—206°, with previous sintering at 203°; when heated with acetic anhydride and sodium acetate, it yields a substance, m. p. 236—237°, which is considered to be an acetyl derivative of the compound $NH{:}C{<}\genfrac{}{}{0pt}{}{NH\cdot C(:NH)}{N{=\!=\!=}CMe}{>}N{\cdot}C_6H_4{\cdot}OH$.

p-*Phenetyldiguanide*, $OEt{\cdot}C_6H_4{\cdot}C_2H_6N_5$, crystallises in colourless leaflets, m. p. 170—172° (decomp.); the hydrochloride (Lumière and Perrin, *loc. cit.*) and *picrate*, m. p. 186—189°, are described. When dissolved in concentrated sulphuric acid and the resulting solution

treated with water, the hydrochloride yields a substance, m. p. 225—226°, to which the author assigns the formula

$$OEt\cdot C_6H_4\cdot NH\cdot CO\cdot NH\cdot C(NH_2)\!:\!NH.$$

Phenetyldiguanide condenses with ethyl oxalate in alcoholic solution, yielding the compound $OEt\cdot C_6H_4\cdot N<\begin{matrix}C(:NH)\cdot NH\cdot C:NH \\ CO\text{———}CO\cdot NH\end{matrix}$, which has m. p. 195—196° (decomp.); it forms *additive* compounds with phenols, and condensation products with formaldehyde and salicylaldehyde. When heated with acetic anhydride and sodium acetate, it yields a *diacetyl* derivative of the triazine base,

$$NH\!:\!C<\begin{matrix}NH\cdot C(:NH) \\ N\text{═══}CMe\end{matrix}>N\cdot C_6H_4\cdot OEt.$$

Ethyl phenyldiguanide-p-carboxylate, $C_2H_6N_5\cdot C_6N_4\cdot CO_2Et$, prepared from ethyl *p*-aminobenzoate, crystallises with one molecule of water in broad-pointed leaflets, m. p. 173°; the anhydrous compound has m. p. 177—178° (decomp.); the *hydrochloride* forms colourless leaflets or prisms; the *picrate* has m. p. 196—197°.

a-*Naphthyldiguanide*, $C_{12}H_{13}N_5$, forms colourless, iridescent leaflets, m. p. 154—155°, and yields a *hydrochloride* and a *picrate*, m. p. 200—203°.

m-*Phenylenebidiguanide*, $C_6H_4(C_2H_6N_5)_2$, prepared from *m*-phenylenediamine hydrochloride, has m. p. 165—167° (decomp.), and yields a *picrate*, m. p. 208—210°.

Diphenylbidiguanide, $C_{12}H_8(C_2H_6N_5)_2$, obtained from benzidine (1 mol.) and dicyanodiamide (2 mols.), has m. p. 241°; the *hydrochloride* and *sulphate* are described.

The interaction of benzidine hydrochloride and dicyanodiamide in equimolecular proportions yields 4'-*amino*-4-*diphenylyldiguanide*,

$$NH_2\cdot C_6H_4\cdot C_6H_4\cdot C_2H_6N_5,$$

which has m. p. 203—204°, and reacts with nitrous acid to form a diazonium compound which couples with α-naphthol, yielding a purple-red *azo*-dye; the *azo*-dyes obtained from β-naphthol, resorcinol, phenol, salicylic acid, and phenylmethylpyrazolone are also mentioned.

Phenyldiguanide-o-carboxylic anhydride,

$$C_6H_4<\begin{matrix}NH\cdot C:NH \\ CO-N\cdot C(NH_2):NH\end{matrix},$$

prepared from anthranilic acid, is a crystalline powder, m. p. above 280°, and forms a sparingly soluble *hydrochloride*.

Phenylmethyldiguanide, $NMePh\cdot C_2H_5N_4$, obtained from methylaniline, crystallises in hygroscopic needles, which decompose when heated.

The interaction of phenylhydrazine hydrochloride and dicyanodiamide yields phenylguanazole (Pellizari, Abstr., 1892, 356), of which the *hydrochloride* and *picrate*, m. p. 225°, are mentioned.

Many of the diguanides described above give characteristic precipitates with potassium ferrocyanide, ammonium molybdate, and with nickel and cobalt salts.

Quantitative experiments on the precipitation of a large number of dyes by means of the diguanide hydrochlorides are also described.

F. B.

Distribution of Auxochromes in Azo-compounds. HUGO KAUFFMANN and W. KUGEL (*Ber.*, 1911, **44**, 2386—2389).—For the study of the effect of the distribution of the auxochromes in azo-compounds (compare Kauffmann and Franck, Abstr., 1906, i, 841), the compounds of the type $N_2[C_6H_3(OMe)_2]_2$, derived from quinol, resorcinol, and catechol, have been compared. These are coloured very differently; the quinol derivative is dark red, that from resorcinol is orange-red or orange, and the catechol derivative is orange-yellow. The rules as to the effect of the positions of the auxochromes therefore apply to azo-compounds. In hydrochloric acid solution the quinol derivative gives a blue, the resorcinol a red, and the catechol a carmine-red coloration.

Resorcinol benzoate couples with diazotised aniline to form *p-benzeneazoresorcinol monobenzoate*, which forms yellow crystals, m. p. 159°, and is hydrolysed to benzeneazoresorcinol, m. p. 169°.

By reduction of nitroresorcinol dimethyl ether with tin and hydrochloric acid, the *hydrochloride* of *aminoresorcinol dimethyl ether* is obtained in long, bluish-white needles. When diazotised, it couples with resorcinol to form 2 : 4-*dimethoxybenzeneazoresorcinol*,

$$C_6H_3(OH)_2\cdot N_2\cdot C_6H_3(OMe)_2,$$

which forms almost black crystals with a green reflex, and is soluble in sodium hydroxide with an orange-yellow coloration, m. p. 186°. Strong hydrochloric acid dissolves it with a dark red, sulphuric acid with a dark blue, coloration.

2 : 4 : 2′ : 4-*Tetramethoxyazobenzene*, $N_2[C_6H_3(OMe)_2]_2$, formed by methylation of the above substance with methyl sulphate, separates in red crystals, m. p. 181°.

3 : 4 : 3′ : 4′-*Tetramethoxyazobenzene* prepared by reduction of nitroveratrole, forms yellow crystals, m. p. 163°.

2 : 5 : 2′ : 5′-Tetramethoxyazobenzene (compare Baessler, Abstr., 1884, 1329) forms dark red crystals, m. p. 142°, soluble in concentrated sulphuric acid with a violet-red, and in hydrochloric acid with a blue, coloration. E. F. A.

Action of Sodium Sulphite and of Sodium Hydrogen Sulphite on Some Azo-dyes. ROBERTO LEPETIT and E. LEVI (*Gazzetta*, 1911, **41**, i, 675—688. Compare Abstr., 1909, i, 569; Nietzki and Helbach, Abstr., 1897, i, 226).—From the reaction between sodium sulphite and nitrobenzeneazosalicylic acid (alizarin-yellow-R) the following substances were isolated: (1) *p*-aminobenzeneazosalicylic acid; (2) *p*-nitroaniline; (3) ammonia; (4) an aminosulphosalicylic acid, to which the formula

$$OH\cdot C_6H_2(NH_2)(CO_2H)\cdot SO_3H,H_2O$$

is ascribed. The last-named substance crystallises in colourless, silky needles (and also in small, compact cubes), which dissolve in alcohol, giving a green, intensely fluorescent solution. The aqueous solution gives a cherry-red coloration with ferric chloride, and reduces ammoniacal silver solutions. Preparation of the substance by sulphonation of aminosalicylic acid shows that the substance is identical with that obtained by Mandt (*Ber.*, 1877, **10**, 1701). It was

s possible to obtain salts with the heavy metals, but the arsenate rystallises in red needles. An acetyl derivative was obtained in the rm of its sodium salt, which crystallises with $1H_2O$. The barium lt also contains $1H_2O$, but is not crystalline.

The action of sodium hydrogen sulphite is more vigorous than that f sodium sulphite, so that, working under the same conditions (in iling water), after one hour most of the dye is decomposed into nitroaniline and aminosulphosalicylic acid without formation of minobenzeneazosalicylic acid.

The reaction between sodium hydrogen sulphite and *p*-aminobenzene-zosalicylic acid (in an autoclave at 130°) proceeds similarly to that st described.

Benzeneazosalicylic acid and sodium sulphite yield (1) a *substance*, hich crystallises in small, brown needles, m. p. 140°, which is ossibly the hydrazo-compound, $NHPh\cdot N(SO_3H)\cdot C_6H_3(OH)\cdot CO_2H$; 2) aminosulphosalicylic acid.

Benzeneazosalicylic acid is more readily acted on by sodium ydrogen sulphite with formation of the following products: 1) aniline; (2) aminosulphosalicylic acid; (3) a substance which ould not be isolated; (4) an *amino*-compound, m. p. 170—173°, hich is a benzidine derivative; (5) a *compound*, m. p. 126—128°, hich contains sulphur but no nitrogen.

Sodium hydrogen sulphite reacts with diphenylbisazosalicylic acid chrysamin G) much less readily than with the preceding compounds. he products isolated were benzidine sulphate and aminosulphosalicylic cid. R. V. S.

Aromatic Nitro-derivatives. II. ROBERTO CIUSA (*Gazzetta*, 911, 41, i, 688—697. Compare Abstr., 1907, i, 874).—The present aper deals with the action of picryl chloride on *cyclo*hexanoneazine nd on benzaldoxime, and the preparation of *cyclo*hexanonemono- and initrophenylhydrazones is described. The author also finds that rinitro-ψ-cumene is strongly dissociated in formic acid solution, so hat a mobile atom of hydrogen is not a necessary condition for the issociability of aromatic polynitro-derivatives. It is suggested that he power of dissociation depends on the presence either of a free ydrogen atom in the nucleus or of a halogen or nitro-group in the rtho-position with respect to another nitro-group.

2 : 4 : 6 : 4′-Tetranitrohydrazobenzene gives a *potassium* salt, $C_{12}H_6O_8N_6K_2$, which crystallises in small, dark needles with a violet heen.

2 : 4 : 6 : 4′-Tetranitrohydrazobenzene when heated with concentrated itric acid yields 2 : 4 : 6 : 4′-*tetranitroazobenzene*,

$$C_6H_2(NO_2)_3N\!:\!N\cdot C_6H_4\cdot NO_2,$$

which forms orange-red needles, m. p. 163—164°. It dissolves in alkalis with difficulty, giving a red coloration.

cyclo*Hexanoneazine* (from *cyclo*hexanone and hydrazine hydrate) has b. p. 165°/25 mm., m. p. 35°. On treatment with picryl chloride, it yields cyclo*hexanonetrinitrophenylhydrazone*, $C_6H_{10}\!:\!N\cdot NH\cdot C_6H_2(NO_2)_3$, which crystallises in flat, red needles, m. p. 133°, and dissolves in alkali, giving a reddish-brown coloration. cyclo*Hexanone*-2 : 4-*dinitro*-

phenylhydrazone, $C_6H_{10}{:}N{\cdot}NH{\cdot}C_6H_3(NO_2)_2$, forms golden-yellow scales, m. p. 145°. cyclo*Hexanone*-p-*nitrophenylhydrazone*,

$$C_6H_{10}{:}N{\cdot}NH{\cdot}C_6H_4{\cdot}NO_2,$$

crystallises in yellowish-brown needles, m. p. 146°; it is insoluble in water, and may be used to detect *cyclo*hexanone in water.

When α-benzaldoxime is heated with picryl chloride in alcoholic solution for two hours, picramide is obtained.

A nitro-group is eliminated from trinitro-ψ-cumene when treated with alkali, and a *potassium* salt, $C_6Me_3(NO_2)_2{\cdot}OK$, can be obtained. By the action of dilute hydrochloric acid, this salt is converted into a yellow *substance*. R. V. S.

Hydrazo-compounds. VII. Methylhydrazotoluene, Methyltolidine, and Ethylbenzidine. BERTHOLD RASSOW and ARM BECKER (*J. pr. Chem.*, 1911, [ii], 84, 329—351. Compare this vol., i, 820, 821).—N-*Methylhydrazo-o-toluene*, $C_6H_4Me{\cdot}NH{\cdot}NMe{\cdot}C_6H_4Me$, prepared by heating a benzene solution of hydrazo-*o*-toluene with excess of methyl sulphate and magnesium oxide for thirty-six to forty hours in an atmosphere of carbon dioxide; it crystallises in rhombic, rectangular, or almost square plates, m. p. 84°.

N-*Methyl*-o-*tolidine*, $NHMe{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}NH_2$, obtained in the form of its *hydrochloride*, $C_{15}H_{18}N_2,2HCl$ (decomp. 260—280°), by the addition of concentrated hydrochloric acid to an alcoholic solution of the preceding compound, has m. p. 85°; it yields an unstable, yellowish-brown *platinichloride*, $C_{15}H_{18}N_2,H_2PtCl_6$, a *picrate*, crystallising in yellow, microscopic needles, which decompose at 184—186°, and a *dibenzoyl* derivative, $NHBz{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}NMeBz$, m. p. 156°; when heated with salicylaldehyde in alcoholic solution, it forms a *salicylidene* derivative, $NHMe{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N{:}CH{\cdot}C_6H_4{\cdot}OH$, which crystallises in needles, m. p. 120°. It reacts with one or two mols. of nitrous acid, yielding (I) 4-*methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*diazonium chloride*, $NHMe{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N_2Cl$, and (II) 4-*methylnitrosoamino*-3 : 3'-*dimethyldiphenyl*-4'-*diazonium chloride*,

$$NO{\cdot}NMe{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N_2Cl.$$

4-*Methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-β-*naphthol*,

$$NHMe{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH,$$

prepared by coupling the diazonium compound (I) with β-naphthol, forms lustrous, dark red crystals, which have m. p. 90—92° and decompose at 120°.

4-*Methylnitrosoamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-β-*naphthol*,

$$C_{20}H_{22}O_2N_4,$$

prepared from (II) and β-naphthol, has m. p. 173°, and is converted into the preceding compound when heated with alcoholic hydrogen chloride.

4-*Methylamino*-3 : 3'-*dimethyldiphenyl*-4'-*azo*-p-*dimethylaniline*,

$$NHMe{\cdot}C_6H_3Me{\cdot}C_6H_3Me{\cdot}N{:}N{\cdot}C_6H_4{\cdot}NMe_2,$$

begins to decompose at 100°, and yields a dark red *hydrochloride*; the *nitroso*-derivative, prepared from (II) and dimethylaniline, forms reddish-yellow, triclinic prisms, which have m. p. 160° and decompose at 180°. It combines with benzenediazonium chloride, yielding 5-*benzeneazo*-4-*methylamino*-3:3'-*dimethyldiphenyl*-4'-*azo*-p-*dimethylaniline*,

NPh:N·C_6H_3Me(NHMe)·C_6H_3Me·N:N·C_6H_4·NMe_2, which decomposes at 180—190°.

Sodium 4-methylamino-3 : 3'-dimethyldiphenyl-4'-azo-β-naphthol-(3 : 6)-disulphonate, $C_{25}H_{21}O_7S_2Na_2$, prepared from the diazonium compound (I) and R-salt, has no definite m. p., and couples with benzenediazonium chloride, yielding *sodium 5-benzeneazo-4-methylamino-3 : 3'-dimethyldiphenyl-4'-azo-β-naphthol-(3 : 6)-disulphonate*,

NPh:N·C_6H_2Me(NHMe)·C_6H_3Me·N:N·$C_{10}H_4(SO_3Na)_2$·OH,

which is dark red and dyes cotton reddish-violet; with diazotised sulphanilic acid it forms a deep bluish-violet *bisazo-dye*.

N-Ethylbenzidine NH_2·C_6H_4·C_6H_4·NHEt, obtained by heating a benzene solution of hydrazobenzene with ethyl sulphate in the presence of magnesium oxide, crystallises in leaflets or needles, m. p. 73—74°.

F. B.

Electrochemistry of Proteins. VII. The Mode of Formation and Ionisation of the Compounds of Proteins with Inorganic Acids and Bases. T. Brailsford Robertson (*J. Physical Chem.*, 1911, **15**, 521—550. Compare this vol., ii, 460).—The author propounds the hypothesis that the combining power of protein for acids and bases resides elsewhere than in the terminal NH_2 and CO_2H groups of the protein chain. The typical group -CO·NH- (alternatively -C(OH):N-) is held to be the seat of the amphoteric properties. The main arguments are as follows.

The soluble neutral hydrochloride of edestin contains nine times as much acid as the insoluble hydrochloride. Hence there must be nine or a multiple of nine basic centres in the edestin molecule. On a probable molecular weight of 7000, nine NH_2 groups correspond with more than 10% of the total nitrogen. In caseinogen the maximum combining capacity for alkali is sixteen times the minimum amount required to render the caseinogen soluble. On a probable molecular weight of 17,600 this requires 12½% of the total oxygen to be in the terminal CO_2H groups. Similar calculations made for egg-albumin also lead to percentages which are too high to be consistent with the catenary structure of the protein molecule.

The non-hydrolysable character of the protein salts is presumptive evidence that they are not ordinary amino-salts or carboxylates in the formation of which water is split off. The anions and cations of caseinogen and ovimucoid salts are protein ions, and the dissociation of potassium caseinogenate is not diminished by potassium chloride.

Burgarski and Liebermann showed (Abstr., 1898, i, 716), by potentiometric methods, that as many chlorine as hydrogen ions are removed from circulation when egg-albumin is dissolved in dilute hydrochloric acid. A mixture of ovimucoid hydrochloride with potassium caseinogenate has at first a conductivity equal to the sum of the conductivities of the constituent solutions, and only very slowly deposits caseinogen as a result of the formation of potassium chloride, since the inorganic constituents of the protein salts are combined in a non-dissociable form.

From analysis of the anodic and cathodic solutions after electrolysis of potassium caseinogenate, the loss of caseinogen from the anodal

region, is about double the loss from the cathodal region. This is in harmony with the assumption that the positive and negative ions of caseinogen are of about equal mass and mobility. The formula of protein being written $R^1C(OH){:}NR^2$, the ionised salts may be written $R^1C(ONa)^{\cdot\cdot} + HN(OH'')R_2$ and $R^1C(OH)^{\cdot\cdot} + HNCl''R^2$ respectively. The ions are assumed to be bivalent from the electrochemical equivalents.

Kossel has drawn attention to the fact that the combining capacity of a protein for acids is proportional to the diamino-acid content, and the combining capacity for bases is proportional to the dicarboxylic acid content. Hence it is probable that the $-C(OH){:}N-$ groups function only when in contiguous pairs. This leads to the formulæ

$$R^1 \Big< \begin{matrix} C(OK)^{\cdot\cdot} + NH(OH'')R^2 \\ C(OK)^{\cdot\cdot} + NH(OH'')R^3 \end{matrix} \quad \text{and} \quad \begin{matrix} R^1C(OH)^{\cdot\cdot} + NHCl'' \\ R^2C(OH)^{\cdot\cdot} + NHCl'' \end{matrix} \Big> R^3$$

for the potassium salt and the hydrochloride of protein respectively.

These formulæ are in agreement with the conductivity and freezing-point determinations in the case of ovimucoid dihydrochloride. Ovimucoid monohydrochloride is supposed to be

$$\begin{matrix} R^1C(OH)^{\cdot\cdot} + HNCl'' \\ R^2C(OH)^{\cdot\cdot} + HN(OH)'' \end{matrix} \Big> R^3.$$

R. J. C.

Precipitation of Protein by Zinc Sulphate. FRITZ LIPPICH (*Zeitsch. physiol. Chem.*, 1911, 74, 360—391).—A detailed discussion of the literature leads to the conclusion that the adsorption hypothesis does not explain adequately the formation of metallic albuminates, and it is undesirable to extend to proteins the conclusions based on experiments made with inorganic colloidal material.

In a series of experiments the proteins of horse-serum were precipitated by increasing quantities of zinc sulphate, and the amount of protein and zinc salt remaining in the filtrate determined, whence the composition of the precipitate could be calculated. It is found that, under certain conditions, the amount of zinc in the precipitate is independent of the concentration of the protein, and also of the initial concentration of the zinc salt. The power of protein to form a zinc salt increases on dilution, but a maximum is soon reached. The results are not in agreement with the adsorption theory, and the change is better represented as a chemical interaction between an amphoteric and a non-amphoteric electrolyte leading to an equilibrium: $ZnSO_4 + 2Na$ protein $\rightleftharpoons Na_2SO_4 + Zn(\text{protein})_2$. The left-hand side of the equation preponderates so long as protein is present in excess, but the amount of precipitate increases on standing, and especially on dilution. When the amount of metallic salt is increased, a point is reached when a sparingly soluble substance is formed, and the reaction is almost entirely in the sense of the equation from left to right. A still further increase in concentration of the metallic salt causes reaction in the opposite direction, and the precipitate will begin to dissolve. For the full discussion of the results the original should be consulted. E. F. A.

What is the Cause of the Separation of Albumin in Bottled Beer which has been Subjected to Normal Treatment in Brewery and Cellar? FRITZ EMSLANDER (*Koll. Chem. Beihefte*, 1911, 3, 47—84).—The conditions favourable to the separation of albumin are discussed with reference to the literature on the subject, and the conclusion is reached that the process is determined primarily by electrochemical effects resulting from the presence of electrolytes. These bring about chemical change in the molecules of albumin, and the transformation is accompanied by alterations in the surface-tension and potential difference between the colloidal particles and the aqueous medium. Coagulation results, and this leads ultimately to turbidity and the deposition of solid substances. H. M. D.

The Hydrolytic Action of Hydrogen Peroxide. CARL NEUBERG and SOICHIRO MIURA (*Biochem. Zeitsch.*, 1911, 36, 37—43).—Hydrogen peroxide in the presence of a manganese or iron salt will bring about at the ordinary temperature the hydrolysis of a number of compounds of high molecular weight. Egg-albumin after treatment yields 10% of its nitrogen as ammonia when heated with magnesia. Substances of an aldehydic and ketonic nature are also formed. Gelatin under similar conditions gives 10·4% of its nitrogen as amide-nitrogen.

Starch, soluble starch, and glycogen are hydrolysed with formation of reducing and fermentable sugars, which yield mixed phenylosazones. Phenylglucosazone is obtained from the products from soluble starch, and phenylmaltosazone from those from glycogen. Inulin gives lævulose.

Yeast nucleic acid gives 23·2% of its nitrogen as amide-nitrogen, and phosphoric acid is set free. With sodium chondroitin sulphate, sulphuric acid is liberated, whilst lecithin yields fatty acids. W. J. Y.

The Reactions between Ferments and Anti-ferments. MARTIN JACOBY (*Biochem. Zeitsch.*, 1911, 34, 485—494. Compare Abstr., 1907, i, 811; ii, 108; 1908, i, 236; ii, 743).—Previous observations that the combination between rennet and anti-rennet of serum is destroyed by acid is confirmed. If acid is allowed to act on serum for some time, the anti-rennet is destroyed. Neither the ferment, anti-ferment, nor the combination are soluble in ether. If rennet solution is shaken, its fermentative action is diminished, and can be neutralised by a smaller quantity of serum. S. B. S.

Action of Oxydases. I. REGINALD O. HERZOG and A. POLOTZKY (*Zeitsch. physiol. Chem.*, 1911, 73, 247—257. Compare Engler and Herzog, Abstr., 1909, ii, 495).—The peroxydase was prepared from sugar beet, and its action in presence of hydrogen peroxide tested on the leuco-base of brilliant-green, on a mixture of *p*-phenylenediamine and dimethylaniline, and on vanillin. Dyes are formed in the first two cases, and a precipitate in the last. The optimum reaction is shown to depend on the concentration of each of the three reacting substances. The change in the case of brilliant-green can be followed colorimetrically. In addition to the formation of colour there is a

bleaching action also brought about by the oxydase. Complete bleaching takes place when the proportion of leuco-base is small compared with that of hydrogen peroxide, provided an excess of enzyme is present. The formation of the dye is much more rapid than the bleaching.

The three possible combinations of mixtures of two of the three reacting substances were prepared and set aside for fourteen hours before the third substance was added. The mixture leuco-base + peroxide reacts the most quickly, that of peroxydase + peroxide is slower, whilst peroxydase + leuco-base shows a marked induction period, and the rate of dye formation is slow. The velocity of the bleaching reaction is much the same for the first and third mixtures, but less for the second. The long induction period indicates that chemical changes, in particular, the formation of additive products, must take place between the components before the formation of colour begins. The experiments indicate that a compound of leuco-base and peroxydase is formed, and that the addition of peroxide displaces the leuco-base and forms a true oxydase from the peroxydase and peroxide. Formation of dye does not take place until the concentration of the active oxydase is sufficient. E. F. A.

Action of Oxydases. II. REGINALD O. HERZOG and A. MEIER (*Zeitsch. physiol. Chem.*, 1911, **73**, 258—265. Compare preceding abstract).—The oxydase extracted from horse-radish was tested against vanillin in presence of hydrogen peroxide, and the amount of dehydrodivanillin formed was weighed. Experiments were made with varying proportions of enzyme and hydrogen peroxide. The filtrate was tested in each case with fresh oxydase solution, and with hydrogen peroxide and guaiacum in order to test whether active peroxydase still remained. The enzyme is destroyed when the relative concentration of hydrogen peroxide is too large; when this is small, the amount of change is approximately proportional to the amount of peroxydase added. The amount of change depends on the proportions of each of the three reacting substances, and the phenomena differ from typical catalysis. The action of peroxydase is classed with the so-called induced reactions. E. F. A.

The Peroxydase of Milk. W. GRIMMER (*Milchw. Zentr.*, 1911, **7**, 395—402).—The peroxydase reaction of fresh milk is shown to be due, not to the presence of inorganic catalysts, but to that of a substance closely connected with the lactalbumin. This is indicated by the similar behaviour of milk-peroxydase and lactalbumin towards precipitating agents and solvents, and, further, by the fact that all compounds which tend to denaturise lactalbumin, such as alcohols, acetone, ether, chloroform, and concentrated acids and alkalis, also lead to the destruction of the enzyme. Putrefaction has the same effect. It is suggested that the enzyme produced in the cells of the mammary gland, and liberated by the destruction of these, is either a protein possessing physical and chemical properties similar to those of lactalbumin, or that it becomes adsorbed by the latter and cannot be separated by ordinary means. H. B. H.

Organic Chemistry.

Catalytic Reactions at High Temperatures and Pressures. XXII. Decomposition of Hexane and *cyclo*Hexane; Isomerisation of *cyclo*Hexane. WLADIMIR N. IPATIEFF and N. DOWGELEWITSCH (*Ber.*, 1911, 44, 2987—2992).—At ordinary pressures, hexane and *cyclo*hexane are decomposed when passed through an iron tube at 650—700°, the decomposition being accelerated by the presence of alumina; hexane decomposes more readily than *cyclo*hexane. The gases thereby produced consist of saturated hydrocarbons, hydrogen, ethylene, propylene, and probably *iso*butylene, whilst the liquid polymerisation product contains a very small proportion of unsaturated hydrocarbons. No hydrocarbons were obtained which reacted with a nitrating mixture or with permanganate.

The course of reaction is quite different under high pressures, taking place at a much lower temperature. With hexane, at 510°, the increase in pressure takes place so rapidly that an explosion occurs, so that *cyclo*hexane only was used in these experiments. It was heated for four hours at 500—510° in the presence of alumina, at a pressure of 110—120 atmospheres; no reaction takes place at this temperature in the absence of alumina. After removal of the ethylene hydrocarbons from the liquid polymerisation product by means of sulphuric acid, the remaining liquid was divided into eleven fractions, none of which decolorised permanganate. The first three fractions, 45—80°, contained polymethylene hydrocarbons, among which was methyl*cyclo*pentane, but no saturated hydrocarbons. The fractions VI—XI, 125—280°, reacted with a nitrating mixture, and therefore contained benzene hydrocarbons; nitro-compounds were also obtained from fractions VI (125—150°) and VII (150—170°). The higher fractions contain polynuclear hydrocarbons as well as saturated hydrocarbons.

Methyl*cyclo*pentane was isolated by refractionation of the first three fractions, and identified by its physical properties and transformation into the nitro-compound. During its formation from *cyclo*hexane there is also the possibility of hexylene being formed, and this compound was also identified. This isomerisation of *cyclo*hexane takes place only at high pressures and in the presence of alumina; at ordinary pressures, even at 760°, no methyl*cyclo*pentane could be found in the products of decomposition. T. S. P.

Polymerisation of Ethylene Hydrocarbons at High Temperatures and Pressures. WLADIMIR N. IPATIEFF (*Ber.*, 1911, 44, 2978—2987).—Both ethylene and *iso*butylene when heated in an iron tube under a pressure of about 70 atmospheres (compare Abstr., 1907, i, 5) undergo rapid polymerisation at 380—400°. The liquid polymerisation products thus obtained consist of mixtures of saturated, ethylenic, and polymethylene hydrocarbons. The fractions boiling below 100° consist chiefly of the saturated and ethylene hydrocarbons, whilst the

polymethylene compounds are found chiefly in the higher-boiling fractions, the proportion being the greater the higher the boiling point. This holds, however, only for fractions boiling below [illegible]; above that temperature hydrocarbons are obtained which are poorer in hydrogen than the polymethylene compounds.

The following compounds were identified in the polymerisation product obtained from ethylene: *iso*pentane, hexane, heptane, octane, nonane, amylene, hexylene, nonanaphthene, α-and β-decanaphthene, hen-deca-, dodeca-, tetradeca- and pentadeca-naphthenes. In the case of *iso*butylene the polymerisation product also contained some hydrocarbons which reacted with a nitrating mixture and with potassium permanganate, and were insoluble in sulphuric acid (D 1·84).

In the presence of alumina the polymerisation of ethylene gives similar results to those obtained in its absence.

At atmospheric pressure ethylene does not polymerise, even at [illegible].

The ethylene hydrocarbons are probably produced by the polymerisation of ethylene itself, or from the polymethylenes by fission of the ring (compare preceding abstract). The saturated hydrocarbons are formed either by the hydrogenisation of the closed-chain hydrocarbons with fission of the ring, or else by fission of the side-chains from the polymethylene nucleus. T. S. P.

Preparation of Sulphurous Acid Derivatives of Unsaturated Hydrocarbons. BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 236386).—When the unsaturated hydrocarbons of general formula $CR_2{:}CR{\cdot}CR{:}CR_2$ (where R is hydrogen, alkyl, or aryl groups) are treated with sulphurous acid, they yield colourless compounds, which when containing a small amount of sulphurous acid are fairly soluble in water, but an increase of the amount renders them insoluble.

When βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene is saturated with sulphur dioxide in aqueous solution, it stiffens to a colourless substance somewhat resembling meerschaum; if shaken for some time with excess of sulphurous acid, an insoluble compound is formed, but if the shaking is interrupted at the right time and the solution carefully evaporated, a *compound* of βγ-dimethylbutadiene with sulphurous acid separates in long needles. The *compound*, prepared from isoprene and sulphurous acid, separates in colourless flakes. F. M. G. M.

α-Iodo-Δ^{δ}-hexene. JULIUS VON BRAUN and H. DEUTSCH (*Ber.*, 1911, **44**, 3062—3065).—The magnesium compound of α-bromo-Δ^{δ}-hexene, $CHMe{:}CH{\cdot}[CH_2]_3{\cdot}MgBr$, obtained by the action of magnesium on αδε-tribromohexane (Braun and Sobecki, this vol., i, 413), is converted by the action of iodine into *α-iodo-Δ^{δ}-hexene*, $CHMe{:}CH{\cdot}[CH_2]_2{\cdot}CH_2I$. This is an almost colourless liquid, b. p. 70—75°/33 mm., and combines with trimethylamine in alcoholic solution, yielding *Δ^{δ}-hexenyltrimethylammonium iodide*, $C_6H_{11}{\cdot}NMe_3I$, m. p. 110°, which is extremely hygroscopic, and at once forms a yellow oil on exposure to air.

By the exhaustive methylation of α-pipecoline, Merling (Abstr., 1891, 1506) obtained a base, $C_6H_{11}{\cdot}NMe_2$, which forms a methiodide isomeric with the above compound, and, accordingly, must have the constitution $CH_2{:}CH{\cdot}[CH_2]_4{\cdot}NMe_2$. F. B.

Specific Gravity of Absolute Ethyl Alcohol at 25°. ANTON KAILAN (*Ber.*, 1911, 44, 2881—2884).—The author finds the density of absolute ethyl alcohol, prepared by distillation of 99·8% alcohol over calcium, to be D_4^{25} 0·78513, which agrees with Winkler's value, 0·78509 (Abstr., 1905, i, 850), within the error of experiment. This necessitates a correction in the water-content of the alcohol used by him in his measurements of the velocity of esterification of organic acids (compare Abstr., 1908, ii, 27, 28, 936), since his previous results were based on Mendeléeff's values for the density of alcohol.

Redeterminations of the velocity of esterification of benzoic acid with hydrogen chloride as catalyst give results in agreement with those obtained by Goldschmidt for alcohol distilled over calcium (Abstr., 1907, ii, 852).

The water-content of alcohol can be determined more accurately by measurement of the density than by measurement of the velocity of esterification, as recommended by Goldschmidt, even when it is less than 0·1%. T. S. P.

Use of Liquid Ammonia in Chemical Reactions. Alkyloxides. E. CHABLAY (*Compt. rend.*, 1911, 153, 819—821. Compare Doby, Abstr., 1903, i, 546; Perkin and Pratt, Trans., 1909, 95, 159).—The preparation of the alkyloxides of alkali earth metals has been realised by bringing about double decomposition between a sodium alkyloxide and the metallic nitrate in liquid ammonia solution. The resulting sodium nitrate, being soluble in the ammonia, can be separated from the alkyloxide. A second method consists in allowing an alcohol to act on a solution of calcium in liquid ammonia, when the action follows the course $2ROH + Ca(NH_3)_4 = Ca(OR)_2 + 4NH_3 + H_2$. A number of barium and strontium alkyloxides have also been prepared in this way. W. O. W.

Catalytic Dehydration of *sec.*- and *tert.*-Pinacolyl Alcohols. FRANÇOIS COUTURIER (*Bull. Soc. chim.*, 1911, [iv], 9, 898—901).—When these alcohols are dehydrated by Sabatier and Senderens' method, using the apparatus designed by Bouveault (Abstr., 1908, i, 117), the secondary alcohol (methyl*tert.*-butylcarbinol),

$$CMe_3\cdot CHMe\cdot OH,$$

gives rise to pinacolin, whilst the tertiary alcohol, dimethyl*iso*propylcarbinol, forms $\beta\gamma$-dimethyl-Δ^{α}-butylene with a small amount of $\beta\gamma$-dimethyl-Δ^{β}-butylene (compare Henry, Abstr., 1907, i, 374; 1909, i, 79, and Delacre, Abstr., 1906, i, 921; 1907, i, 459). These results support Delacre's view that *sec.*-pinacolyl alcohol is not readily isomerised, and are in opposition to Henry's results (*loc. cit.*), which indicate that the haloid esters of this alcohol undergo isomerisation when heated (Abstr., 1908, i, 881). T. A. H.

Accessory Products in the Hydrolysis of (I.) Crude Pinacone; (II.) Pure Pinacone. MAURICE DELACRE (*Bull. Soc. chim.*, 1911, [iv], 9, 885—889, 889—898).—A detailed revision of the work done by Couturier (Abstr., 1893, i, 244) and by Richard and Langlais (Abstr., 1910, i, 462) on the identification of the by-products formed in the preparation of pinacolin from pinacone.

From 10·3 kilograms of residues from the preparation of pinacolin from crude pinacone, 6·277 kilograms of material boiling at 200—220° were obtained, the remainder, after allowing 2·27 kilograms for residue and loss, being divided into eleven fractions boiling between 140° and 200°. From the portion b. p. 200—220°, two fractions, b. p. 213—214° and 214·5—218°, were isolated. The first of these had approximately the composition $C_9H_{14}O$, and gave an oxime, m. p. 161°, and a semicarbazone, m. p. 187°. A portion of this fraction boiling at 214°, on the contrary, gave with hydroxylamine two substances, of m. p. 60° and 88° respectively. The fraction is therefore a mixture, and it is impossible at present to say whether it contains *iso*phorone and deoxymesitylic oxide (Harries and Hubner, Abstr., 1897, i, 549). In the low boiling portion of the residues, di*iso*propenyl (Abstr., 1896, i, 591) and a hydrocarbon, C_7H_{14}, b. p. 60—63°, were found.

In the second paper details are given of a still more exhaustive fractionation of by-products from the preparation of pinacolin from crude pinacone. No mesitylene could be detected, but a substance, $C_9H_{14}O$, b. p. 210° (approx.), giving an oxime, m. p. 75°, and a semicarbazone, m. p. 196°, was obtained; this may be *iso*phorone or a new isomeride of this substance. A similar examination of the by-products resulting from the preparation of pinacolin from pure pinacone gave analogous results. T. A. H.

Autoxidation of Aliphatic Amino- and Polyhydroxy-derivatives. II. WILHELM TRAUBE (*Ber.*, 1911, **44**, 3141—314[illegible]. Compare Abstr., 1910, i, 294).—Cuprammonium oxide and the complex copper salts of aliphatic amino- and hydroxy-compounds are autoxidisable. The experiments with the latter have now been made with barium hydroxide instead of sodium hydroxide, the alkali being saturated with cupric hydroxide and oxidation effected at about 70°. Under these conditions carbon dioxide is formed in considerable quantity, and oxalic acid appears as well as formic acid.

Glycerol is oxidised to the extent of about 20% to carbon dioxide and oxalic acid, $C_3H_8O_3 + O_6 = C_2H_2O_4 + CO_2 + 3H_2O$, and about 80% to formic and oxalic acids, $C_3H_8O_3 + O_5 = C_2H_2O_4 + H_2CO_2 + 2H_2O$.

The oxidation of glyceric acid, barium gluconate, glycollic acid, glycine, and lactic acid has been studied in like manner.

E. F. A.

αβδ-Trihydroxybutane; its Conversion into Furan Derivatives and Erythritol. HENRI PARISELLE (*Ann. Chim. Phys.*, 1911, [viii], **24**, 315—410).—This paper gives a detailed, connected account of results already published (Abstr., 1908, i, 496; 1909, i, 282, 691; 1910, i, 353, 463), adding new data regarding certain of the substances described, and giving comparisons of allylcarbinol with allyl alcohol and of αβδ-trihydroxybutane with αβγ-trihydroxybutane and glycerol.

Allylcarbinol, D^{17} 0·848, n_D^{17} 1·421, prepared as described already (Abstr., 1909, i, 282), on treatment with phosphorus tribromide or hydrogen bromide furnishes some αγ-dibromobutane along with a poor yield of the corresponding *bromide* [*bromo-Δ^a-butylene*],

$$CH_2{:}CH{\cdot}CH_2{\cdot}CH_2Br,$$

D^0 1·355, D^{17} 1·33, n_D^{17} 1·465, b. p. 97—99°/760 mm., which on treatment

with solid potassium hydroxide gives $\Delta^{\alpha\gamma}$-butadiene, $CH_2{:}CH{\cdot}CH{:}CH_2$, identified by conversion into tetrabromobutane, m. p. 117—118° (see below). The acetate has D^0 0·93, D^{18} 0·918, n_D^{15} 1·411, and readily combines with bromine to form γδ-dibromobutyl acetate, D^{18} 1·73, n_D^{18} 1·508, b. p. 135°/16 mm. (compare Wagner, Abstr., 1894, i, 563). Butylcarbinol formal, $CH_2(O{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH_2)_2$, has D^0 0·897, D^{18} 0·88, n_D^{15} 1·4333 (Abstr., 1909, i, 282).

The methyl ether of allylcarbinol, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, D^0 0·817, D^{20} 0·8, n_D^{20} 1·398, b. p. 68—69°, was prepared by the action of zinc dust in alcohol on γδ-dibromobutyl methyl ether, n_D^{20} 1·5158, b. p. 56°/16 mm. (compare Lespieau, Abstr., 1907, i, 580). γδ-Dibromobutyl ethyl ether, D^0 1·662, D^{20} 1·614, n_D^{20} 1·498, b. p. 98°/12 mm. (compare Abstr., 1910, i, 353), on treatment with hydrogen bromide forms only βδ-dibromobutane, D^{20} 1·80, n_D^{20} 1·507, b. p. 64°/13 mm. (compare Demjanoff, Abstr., 1895, i, 161). The *phenylurethane* of allyl alcohol has m. p. 70° and is crystalline; that of allylcarbinol is a syrup.

αβδ-Tribromobutane, D^0 2·276, D^{18} 2·234, n_D^{15} 1·574, prepared as described already (Abstr., 1908, i, 496), when heated with boiling water or moist silver oxide gives 3-hydroxytetrahydrofuran (Abstr., 1909, i, 691), D^0 1·107, D^{18} 1·07, n_D^{15} 1·4478, MR 21·91 (calc., 21·61), a colourless, syrupy liquid, and with potassium acetate solution yields the triacetin of αβδ-trihydroxybutane, D^0 1·152, D^{18} 1·13, n_D^{18} 1·436, b. p. 150°/11 mm., or 158°/17 mm., which on hydrolysis by baryta gives the trihydric alcohol, D^0 1·21, D^{20} 1·18, n_D^{20} 1·47, b. p. 179°/13 mm. (compare Wagner, *loc. cit.*). This yields a *triphenylurethane*, m. p. 149—152°, in colourless needles, and a *δ-ethyl ether*, D^0 1·08, n_D^{15} 1·45, b. p. 130°/14 mm., of which the *diphenylurethane* is crystalline, and melts at 98—99°. In the formation of this ether, as in that of the methyl ether, some 3-hydroxytetrahydrofuran is formed (Abstr., 1909, i, 691). γδ-Dibromobutyl alcohol, D^0 2·02, D^{15} 1·98, n_D^{15} 1·548, b. p. 114°/11 mm. (compare Wagner, *loc. cit.*, and Abstr., 1909, i, 282), gives a *phenylurethane*, m. p. 70—71°. α-Bromo-Δ^{γ}-butylene oxide with (1) potassium acetate gives the diacetin of αβδ-trihydroxybutane (Abstr., 1909, i, 691), D^0 1·17, D^{16} 1·15, n_D^{16} 1·446, b. p. 161—163°/18 mm.; (2) acetic anhydride and zinc chloride yields *α-bromo-γδ-diacetoxybutane*, $CH_2Ac{\cdot}CHAc{\cdot}CH_2{\cdot}CH_2Br$, D^{20} 1·44, n_D^{20} 1·473, b. p. 140—141°/13—14 mm., a colourless liquid, having an odour like that of ethyl acetate, and (3) with potassium acetate furnishes α-acetoxy-Δ^{γ}-butylene oxide, $\left.\begin{matrix}CH_2\\ O\end{matrix}\right>CH{\cdot}CH_2{\cdot}CH_2{\cdot}OAc$, D^{18} 1·12, n_D^{18} 1·446, b. p. 189—192°, a colourless liquid having an odour recalling that of ethyl acetate. α-Ethoxy-Δ^{γ}-butylene oxide, D^0 0·957, D^{18} 0·934, n_D^{18} 1·415 (Abstr., 1910, i, 353), is converted by hydrogen chloride into α-chloro-β-hydroxy-δ-ethoxybutane.

Δ^{α}-Butylene-γδ-oxide, $\left.\begin{matrix}CH_2\\ O\end{matrix}\right>CH{\cdot}CH{:}CH_2$, precipitates a solution of magnesium chloride in alcohol and water, polymerises readily, is easily hydrated to form erythrol, from which natural and racemic erythritols may be prepared (compare Abstr., 1910, i, 463), and on

treatment with bromine in chloroform gives *αβ-dibromo-Δγ-butylene oxide*, D^0 2·028, n_D^{22} 1·542, b. p. 99°/13—14 mm. The latter with hydrogen bromide in chloroform gives *αγδ-tribromo-β-hydroxybutane*, b. p. 148—150°/14 mm. This in turn reacts with phosphorus pentabromide at 150° to give *αβγδ-tetrabromobutane*, m. p. 117—119°, crystallising in colourless needles (compare Griner, Abstr., 1893, 227). Ciamician and Magnaghi's form of this substance, m. p. 38—39° (Abstr., 1886, 521), was not obtained. By the action of bromine on erythrol [Δ^{α}-butylene-γδ-diol], two αβ-dibromo-γδ-dihydroxybutanes, the one crystalline, m. p. 88—89·5°, and probably identical with that of Grimaux and Cloez (Abstr., 1890, 730) and the other liquid, are formed.
T. A. H.

Chloro-ethers. VI. αβ-Dichloro-n-propyl Ether, αββ′-Trichloro-n-propyl Ether, and Tetrachloro-n-propyl Ether. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1911, 41, ii, 224—243. Compare Oddo and Mameli, Abstr., 1904, i, 280; 1906, i, 134, 619, and the two following abstracts).—In the present paper the authors continue the study of the above dichloro- and trichloro-ethers, recording new decomposition products and condensations, and describe also a tetrachloro-ether.

In the chlorination of *n*-propyl ether in diffuse light at 25°, in addition to the dichloro-ether, the following substances are produced in small quantities: (1) α-monochloropropaldehyde; (2) a substance, b. p. 144—147°, probably a *monochloropropyl ether*; (3) the trichloro-ether. When the dichloropropyl ether is treated with sulphuric acid at 135—140°, α-chloropropaldehyde, b. p. 85—86°, is obtained (compare Brochet, Abstr., 1896, i, 114). This aldehyde polymerises readily on keeping (although it is stable in a sealed tube); the *polymeride* is a white powder, which does not melt, but is reconverted into the liquid aldehyde at 170—200°. It appears to form a compound with water, but the hydrate could not be obtained in a crystalline state. It also forms an alcoholate with propyl alcohol, but this also was not isolated.

When αβ-dichloro-*n*-propyl ether is boiled with water and the product fractionated, α-chloropropaldehyde and β-chloropropacetal, $CHMeCl\cdot CH(OPr)_2$, are obtained. The action of propyl alcohol also results in the formation of the latter substance.

When αβ-dichloro-*n*-propyl ether is boiled for about one hundred hours, n-*propyl-β-chloropropylene ether*, $CMeCl\!:\!CH\cdot OPr$, is obtained as a colourless liquid, b. p. 145—146·5°. The action of bromine on this unsaturated compound yields *β-chloro-αβ-dibromopropyl ether*,

$$CMeClBr\cdot CHBr\cdot OPr,$$

which is a mobile liquid, b. p. 140—142°/20 mm. With pyridine it yields a *compound*, m. p. 216—217°, which gives a *platinichloride*, m. p. also 216—217°.

In view of the above reactions it is shown that the dichloro-ether is αβ-dichloro-*n*-propyl ether, and this is confirmed by its synthesis from α-chloropropaldehyde, propyl alcohol, and hydrogen chloride.

αββ′-Trichloro-*n*-propyl ether is obtained mixed with the tetrachloro-ether by chlorinating *n*-propyl ether or αβ-dichloro-*n*-propyl

...her on a boiling brine-bath; it has b. p. 115—120°/5—10 mm. When heated with sulphuric acid it yields α-chloropropaldehyde; with carbamide or urethane it gives the same products as the dichloro-ether. One chlorine atom is removed by silver nitrate, showing that this occupies the α-position, and this is confirmed by its behaviour with pyridine, which yields a compound of which the *platinichloride* (orange-yellow crystals, m. p. 187°) has the composition

$$(C_6H_{11}OCl_3{\cdot}C_5H_5N)_2PtCl_4.$$

The constitution of the trichloro-ether follows from these reactions, from its modes of formation, and from its synthesis from β-chloropropaldehyde, allyl alcohol, and hydrogen chloride.

The *tetrachloro*-n-*propyl ether* obtained in the preparation of the trichloro-ether is a colourless, oily liquid, b. p. 157—162°/5—10 mm. With sulphuric acid and with silver nitrate, it behaves like the mono- and di-chloro-ethers. It gives a pyridine compound, of which the *platinichloride*, $(C_6H_{10}OCl_4,C_5H_5N)_2,PtCl_4$, forms orange-yellow crystals, m. p. 187°. R. V. S.

Chloro-ethers. VII. Aldehydic Condensations by means of Halogenated Ethers. GIUSEPPE ODDO and GUIDO CUSMANO (*Gazzetta*, 1911, 41, ii, 246—258. Compare preceding abstract).—Carbamide reacts with dichloroacetaldehyde or its polymeride in aqueous solution, yielding *α-hydroxy-ββ-dichloroethylcarbamide*, which forms crusts of prismatic crystals, m. p. 142° (decomp.). αββ-Trichloroethyl ether and carbamide in presence of sodium acetate yield the same condensation product.

Hydrazine hydrate reacts with dichloroacetaldehyde, with its polymeride, and with αββ-trichloroethyl ether, giving an amorphous, reddish-yellow powder, which does not melt at 300°.

Semicarbazide reacts with the same three ethers, yielding a substance, $C_4H_5O_2N_5$, which is an amorphous, yellowish-white powder.

Phenylhydrazine with dichloroacetaldehyde or αββ-trichloroethyl ether forms glyoxalosazone.

Carbamide and α-chloropropaldehyde yield a white, amorphous substance, m. p. 167—170° (decomp.), which is also formed when carbamide reacts with αβ-dichloro-, αββ′-trichloro-, or tetrachloro-*n*-propyl ether.

Urethane reacts with α-chloropropaldehyde, αβ-dichloro-, αββ′-trichloro- and tetrachloro-*n*-propyl ether, giving in all cases *β-chloropropylidenebisurethane*, $CHMeCl{\cdot}CH(NH{\cdot}CO_2Et)_2$, which forms tufts of long, colourless needles, m. p. 122—123°.

Urethane and β-chloro-αβ-dibromo-*n*-propyl ether yield *β-chlorobromopropylidenebisurethane*, $CMeClBr{\cdot}CH(NH{\cdot}CO_2Et)_2$, which crystallises in small, transparent prisms, m. p. 113—115°. The above chlorobromo-ether, when treated with carbamide, gives an aldehydic compound crystallising in minute needles, m. p. 183—184°.

R. V. S.

Catalytic Actions of Sulphuric Acid. I. GIUSEPPE ODDO (*Gazzetta*, 1911, 41, ii, 258—267. Compare preceding abstracts).—When the halogenated ethers and some related substances are dropped

on concentrated sulphuric acid at a high temperature, the corresponding aldehydes are formed.

[With Efisio Mameli.]—Dichloroacetaldehyde is obtained from any of the following substances when dropped on concentrated sulphuric acid at 140—145°: $\alpha\beta\beta$-trichloroethyl ether, dichloroacetaldehyde hydrate, dichloroacetal, and ethyl dichlorovinyl ether (compare Abstr., 1904, i, 280; Wohl and Roth, Abstr., 1907, i, 170).

[With Guido Cusmano.]—α-Chloropropaldehyde is obtained by the action of concentrated sulphuric acid at 135—140° on the following substances: $\alpha\beta$-dichloro-, $\alpha\beta\beta'$-trichloro- and tetrachloro-*n*-propyl ether, di-*n*-propyl-β-chloropropylidene ether, and *n*-propyl-β-chloropropylene ether.

[With Eugenia Mantovani.]—When ethyl acetoacetate is dropped on sulphuric acid at 155—165°, keten appears to be formed, but is resinified by the acid; at the same time much ethyl acetate is produced. The decomposition of ethyl malonate with sulphuric acid at 200° yields carbon dioxide, ethylene, and ethyl acetate. Ethyl succinate is not acted on below 240—250°, and is then merely hydrolysed, ethyl alcohol and succinic acid being obtained.

R. V. S.

Nitrogen and Sulphur Derivatives of Carbon Disulphide. XVIII. Chlorothiocarbonates.

Marcel Delépine (*Bull. Soc. chim.*, 1911, [iv], 9, 901—903. Compare Klason, Abstr., 1887, 1029).—The methyl, ethyl, and propyl esters have been prepared by Klason's method (*loc. cit.*) and are described.

The alcohol (2 mols.) is added gradually to thiocarbonyl chloride at atmospheric temperature, and after twelve to twenty-four hours ether is added, and finally water. The oily layer is separated, washed with water, dried over calcium chloride, and rectified by distillation in carbon dioxide. The yield of the methyl and ethyl esters is about 50% of the theoretical, but is very small in the case of the propyl ester. The esters are pale yellow liquids of pungent ozone-like odour; they fume in the air, owing to oxidation and the liberation of sulphuric acid; they are luminous in the dark, the propyl ester being less luminous. With amines they react according to the equation: $2R_1R_2NH + Cl\cdot CS\cdot OR' = R_1R_2N\cdot CSOR' + R_1H_2NH,HCl$, where R_1 or R_2 may be a hydrogen atom. With secondary amines they give dialkylthiocarbamates (Abstr., 1910, i, 720).

Methyl chlorothiocarbonate, CSCl·OMe, has D_4^0 1·2975, $D_4^{..}$ 1·26.., and b. p. 107—108°. Ethyl chlorothiocarbonate has D_4^0 1·21.., D_4^{18} 1·1955, b. p. 127—128° (compare Klason, *loc. cit.*). *Propyl chlorothiocarbonate*, CS·Cl·OPr$^{\alpha}$, b. p. 148—151°, reacts with aniline to form propyl phenylthiocarbamate (Orndorff and Richmond, Abstr., 1900, i, 156), which is best obtained by Roschdestvensky's method (Abstr., 1909, i, 300).

T. A. H.

Some Compounds of Organic Salts of Bivalent Metals with Ammonia, Pyridine, and Phenylhydrazine.

Hermann Grossmann and Gustav Jäger (*Zeitsch. anorg. Chem.*, 1911, 73, 48—74).—For the purpose of investigating the influence of the acid radicle on the type of additive compound formed by salts (compare Grossmann

nd Hänsler, Abstr., 1906, i, 7), the additive compounds of a number f salts of organic acids have been prepared. The ammonia compounds are usually prepared by dissolving the hydrated salt in 25% queous ammonia, filtering, and evaporating, first on a water-bath and hen in a desiccator over sodium hydroxide in an atmosphere of mmonia.

Ammonia cupric formate, $Cu(HCO_2)_2,3NH_3$, forms large, blue risms or slender needles, m. p. 154°. The compound is stable in air, ut is decomposed by water. *Ammonia cupric chloroacetate*,

$$Cu(CH_2Cl\cdot CO_2)_2,2NH_3,H_2O,$$

orms a blue, crystalline powder, m. p. 180° (decomp.). *Ammonia upric trichloroacetate*, $Cu(CCl_3\cdot CO_2)_2,5NH_3$, forms dark bluish-violet rystals, which lose ammonia suddenly, becoming grass-green at 94° nd melting at 98°. After six weeks in air the crystals contain NH_3. *Ammonia zinc formate*, $Zn(HCO_2)_2,2\frac{1}{2}NH_3$, forms colourless, rismatic needles, m. p. 126°. *Ammonia zinc acetate*,

$$Zn(C_2H_3O_2)_2,6NH_3,5H_2O,$$

orms colourless needles. *Ammonia cadmium formate*,

$$Cd(HCO_2)_2,3NH_3,3H_2O,$$

orms transparent crystals, m. p. 70°, and loses NH_3 and H_2O in air. *Ammonia cadmium acetate*, $Cd(C_2H_3O_2)_2,4NH_3$, forms transparent ubes, m. p. 141°, and loses NH_3 in air. *Ammonia nickel formate*, $Ni(HCO_2)_2,3NH_3,2H_2O$, is a bright blue, crystalline powder, becoming reen at 120° and charring at 360°, three other additive compounds of he salt being also obtained, containing $4NH_3,2H_2O$, $3NH_3,H_2O$, nd $2NH_3$ respectively. *Ammonia nickel acetate*, $Ni(C_2H_3O_2)_2,2NH_3$, s a green precipitate; a definite compound could not be obtained from the chloroacetate. *Ammonia nickel trichloroacetate*,

$$Ni(CCl_3\cdot CO_2)_2,3NH_3,3H_2O,$$

forms blue crystals, and becomes green in air, losing $2NH_3$ and $3H_2O$.

Pyridine cupric formate, $Cu(HCO_2)_2,3C_5NH_5$, forms blue needles, m. p. 103°, and loses pyridine in air. Two *pyridine cupric acetates* are obtained, $Cu(C_2H_3O_2)_2,5C_5NH_5$ being bright green, and

$$Cu(C_2H_3O_2)_2,6C_5NH_5$$

dark violet. *Pyridine cupric chloroacetate*,

$$Cu(CH_2Cl\cdot CO_2)_2,2C_5NH_5,2H_2O,$$

forms blue crystals, and a second compound is also obtained. *Pyridine cupric trichloroacetate*, $Cu(CCl_3\cdot CO_2)_2,4C_5NH_5,2H_2O$, forms sky-blue needles. *Pyridine zinc formate*, $Zn(HCO_2)_2,2C_5NH_5$, loses pyridine in air, whilst zinc acetate yields only unstable products. *Pyridine cadmium formate*, $Cd(HCO_2)_2,3C_5NH_5$, has m. p. 94°, and loses pyridine in air. *Pyridine nickel formate*, $Ni(HCO_2)_2,3C_5NH_5$, is a pale green, crystalline powder, which blackens without melting; *pyridine cobalt formate*, $Co(HCO_2)_2,3C_5NH_5$, is pale pink, and is stable in air, but loses pyridine after some months.

Phenylhydrazine zinc formate, $Zn(HCO_2)_2,2C_6H_8N_2$, is a white solid, m. p. 110°, which rapidly darkens in air. *Phenylhydrazine cadmium formate*, $Cd(HCO_2)_2,C_6H_8N_2$, has m. p. 128°; *phenylhydrazine nickel formate*, $Ni(HCO_2)_2,C_6H_8N_2,3H_2O$, a bluish-green, amorphous mass, blackens without melting, a blue product being also obtained, probably containing $2C_6H_8N_2$. *Phenylhydrazine cobalt formate*, $Co(HCO_2)_2,2C_6H_8N_2$,

is a pink substance, m. p. 170—172°, which darkens in air. *Phenylhydrazine cobalt acetate*, $Co(C_2H_3O_2)_2,4C_6H_8N_2$ (compare Moitessier, Abstr., 1897, i, 561), is unstable; *phenylhydrazine cobalt chloroacetate*, $Co(CH_2ClCO_2)_2,3C_6H_8N_2$, and *phenylhydrazine cobalt trichloroacetate*, $Co(CCl_3CO_2)_2,6C_6H_8N_2$, m. p. 188°, are pink solids. A tabular summary of the compounds of this series is given. C. H. D.

The Hydrates of Potassium Acetate, their Solubility and Transition Point. RYUJI ABE (*Mem. Coll. Sci. Eng. Kyoto*, 1911, 3, 211—215).—The solubility curve of potassium acetate in water has a single break at 41·3°, the stable phase at lower temperatures being $2KC_2H_3O_2,3H_2O$, and at higher temperatures, $2KC_2H_3O_2,H_2O$. C. H. D.

Aliphatic Nitro-compounds. XI. α-Nitroisobutyric Acid. WILHELM STEINKOPF and ALEXANDER SUPAN (*Ber.*, 1911, 44, 2891—2897).—α-Nitroisobutyric acid has been prepared by the following series of operations: α-Hydroxylaminoisobutyronitrile, obtained by the addition of hydrogen cyanide to acetoxime, was oxidised with potassium permanganate in sulphuric acid to α-nitroisobutyronitrile (Piloty, Abstr., 1898, i, 616). This cannot be hydrolysed directly, but on heating with methyl alcohol and hydrochloric acid, it is converted almost quantitatively into the hydrochloride of nitroisobutyroiminomethyl ether,

$$NO_2\cdot CMe_2\cdot C(NH)\cdot OMe,HCl.$$

This is decomposed by water into methyl-α-nitroisobutyrate, $NO_2\cdot CMe_2\cdot CO_2Me$, a colourless oil, which with ammonia forms α-nitroisobutyramide, and when left for some days with concentrated hydrochloric acid is slowly hydrolysed to α-nitroisobutyric acid.

When the ammonium salt is treated with sodium nitrite and sulphuric acid, carbon dioxide is eliminated and a blue oil formed, which solidifies to colourless crystals of propyl ψ-nitrol,

$$NO\cdot CMe_2\cdot NO_2.$$

α-Nitroisobutyric acid differs from nitroacetic and α-nitropropionic acids in not being hygroscopic. On prolonged keeping, it decomposes to a blue oil mixed with colourless crystals, which melt to a blue liquid, and nitrous acid is liberated. This is a nitroso-compound, but it has not at present been identified. When fused, α-nitroisobutyric acid liberates carbon dioxide and forms a colourless oil, which suddenly decomposes, becoming blue and solidifying to a colourless solid. Similar changes are noted on heating in solvents. Possibly the acid decomposes into *sec.-aci*-nitropropane, this into acetone and nitrosyl, which re-unite to a nitroso-alcohol, $NO\cdot CMe_2\cdot OH$.

α-Nitroisobutyronitrile is an oil, b. p. 73°/12 mm. *Methyl-α-nitroisobutyric acid* has b. p. 73—74°/12 mm. *α-Nitroisobutyric acid* forms crystals, m. p. 95°; the *ammonium*, *sodium*, and *phenylhydrazine* salts have been prepared. E. F. A.

Action of Hydrogen Chloride and Methyl Alcohol on Negatively Substituted Nitriles. WILHELM STEINKOPF and WIATSCHESLAW MALINOWSKI (*Ber.*, 1911, 44, 2898—2904).—Whilst

[Ha]user has shown that, in general, both aromatic and aliphatic imino-[et]her hydrochlorides are obtained by the reaction of nitrile, alcohol, [an]d hydrogen chloride, Steinkopf obtained trichloroacetamide from [tr]ichloroacetonitrile (Abstr., 1907, i, 488) and nitroacetamide from [n]itroacetonitrile (Abstr., 1909, i, 216), instead of the expected imino-[e]thers. On the other hand, Steinkopf and Supan (preceding abstract) [fou]nd that α-nitroisobutyronitrile gives the normal imino-methyl ether [an]d not the amide. The influence of the negative nitro-group appears [t]o be less when the nitro-group is tertiary.

The behaviour of a number of halogen substituted acetonitriles [to]wards methyl alcohol and hydrogen chloride has now been [i]nvestigated. Chloro-, bromo- and iodo-acetonitrile give the normal imino-ether hydrochloride; dibromoacetonitrile yields a mixture of imino-ether and dibromoacetamide.

Dichloro-, trichloro-, dichloronitro-, and tribromo-acetonitrile all yield the corresponding amides, no trace of imino-ether being formed.

The primary nitro-group is as active as two or three chlorine atoms; this is probably owing to its reacting in the *aci*-form.

With trichloroacetonitrile and dimethylethylcarbinol only the corresponding amide was obtained. The imino-ether could not be obtained on boiling tribromoacetonitrile with methyl alcohol.

[With ALEXANDER SUPAN.]—ω-*Nitrophenylacetonitrile* was obtained pure in colourless crystals, m. p. 39—40°, from the sodium salt (Wislicenus, Abstr., 1902, i, 541).

E. F. A.

Oxidation of Hexoic and Heptoic Acids by Dilute Permanganate Solutions. E. S. PRSCHEVALSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1000—1006).—Oxidation of *n*-hexoic acid with 1% neutral permanganate solution in the cold yields butyric, valeric, oxalic, and succinic acids.

Under similar conditions, *n*-heptoic acid gives oxalic, succinic, propionic, butyric, and valeric acids; further, the action of semicarbazide hydrochloride on that portion of the oxidation products which dissolves readily in ether, water, alcohol, chloroform, and acetone yields two isomeric semicarbazones, $C_8H_{15}O_3N_3$, one, m. p. 138—140°, readily soluble, and the other, m. p 176°, slightly soluble. These represent semicarbazones of a keto-acid, $C_7H_{12}O_3$, which must be regarded as an intermediate product in the oxidation of *n*-heptoic acid.

T. H. P.

Preparation of Diglycollic Acid Esters of Phenols and Phenolic Derivatives. C. F. BOEHRINGER & SÖHNE (D.R.-P. 236045).—Phenolic esters of diglycollic acid prepared from the acid dichloride have been described (Abstr., 1910, i, 732); it is now found that this reaction proceeds smoothly with the acid on gently warming in the presence of phosphorus pentachloride and an indifferent base, the phenyl ester being thus obtained in 90% yield. The *o*-*tolyl* ester has m. p. 100—101°.

F. M. G. M.

Studies on Tautomerism. VI. Colorimetric Method for the Estimation of Enols in Allelotropic Mixtures. LUDWIG KNORR and H. SCHUBERT (*Ber.*, 1911, **44**, 2772—2778. Compare Wislicenus, Abstr., 1900, i, 9, 597).—By colorimetric comparison of the solutions obtained on adding ferric chloride to equilibrium mixtures of tautomeric substances, the amount of enolic form present can be estimated. The maximum coloration is produced when 1 mol. of ferric chloride reacts with the enol, the corresponding equation being $RH + FeCl_3 = FeRCl_2 + HCl$, where R is the enolic residue. Standard solutions of three kinds are employed: (1) when the pure enolic form is available, a solution of it containing an equimolecular quantity of sublimed ferric chloride; (2) solutions of the iron salts of the type FeR_3 (see below), to which 2 mols. of ferric chloride have been added ($FeR_3 + 2FeCl_3 = 3FeCl_2R$), and in addition, to make them identical with those of the first type, 3 mols. of hydrochloric acid; (3) solutions (usually alcoholic) of equilibrium mixtures to which 1 mol. of ferric chloride has been added, the amount of the enolic form present having been determined by comparison with test solutions of one of the first two types. The standard solutions of the third kind often remain unaltered for months. The solutions of types I. and II. also suffer no marked alteration on keeping, unless (as in the case of dibenzoylacetylmethane, for instance) decomposition occurs; hence the enolic forms may be fixed in the form of their iron salts. In some cases (ethyl acetoacetate and especially ethyl benzoylacetate) the addition of hydrochloric acid to the iron salts lessens the intensity of colour of the solution; in other cases (tribenzoylmethane) no change is observed. The standard solutions of the second type have exactly the same degree of coloration as those of type I.

The method has been employed for the study of the diacetylsuccinic ester, mesityl-oxide-oxalic esters, and Claisen's triketones. In the present paper experimental data are given in the case of methyl mesityl-oxide-oxalate. In the fused state at 98° the enolic ester reaches equilibrium (4% enol) after twenty-five hours, whilst the ketonic ester attains to the same equilibrium in two hundred hours. In absolute alcoholic solution at 78° equilibrium is reached (3·7% enol) after twelve days, whilst the ketonic form contains 3·9% enol after twenty days. In absolute alcohol at room temperature, the enolic ester is converted into the equilibrium mixture (4% enol) after eight weeks. Determinations were also made of the equilibria reached in different solvents after fourteen days at 80°.

Some new iron salts have been prepared (compare Hantzsch and Desch, Abstr., 1902, i, 708; also this vol., i, 976). *Ethyl ferriacetoacetate*, $Fe(C_6H_9O_3)_3$ (from an alcoholic solution of ethyl sodioacetoacetate and an ethereal solution of ferric chloride), forms small, compact, red crystals, m. p. 99—100°. The solutions of the salt are orange-coloured, and become cherry-red on addition of ferric chloride.

Ethyl ferriformylphenylacetate, $Fe(C_{11}H_{11}O_3)_3$, is obtained in a crystalline condition by treating an ethereal solution of the ester with

in alcoholic solution of sodium ethoxide and ferric chloride in the presence of sodium acetate. R. V. S.

Lactarinic Acid. J. BOUGAULT and CHARLES CHARAUX (*Compt. rend.*, 1911, **153**, 880—881. Compare this vol., i, 835).—Lactarinic acid is identical with ε-*ketostearic acid*,

$$CH_3\cdot[CH_2]_{11}\cdot CO\cdot[CH_2]_4\cdot CO_2H,$$

since it undergoes the Beckmann transformation, giving rise to two compounds, $CH_3\cdot[CH_2]_{11}\cdot NH\cdot CO\cdot[CH_2]_4\cdot CO_2H$ and

$$CH_3\cdot[CH_2]_{11}\cdot CO\cdot NH\cdot[CH_2]_4\cdot CO_2H.$$

These were not isolated, but recognised by the products obtained on hydrolysis. W. O. W.

Synthesis of Fumaric and Maleic Acids from the Acetylene Di-iodides. EDWARD H. KEISER and LEROY MCMASTER (*Amer. Chem. J.*, 1911, **46**, 518—523).—Keiser (Abstr., 1890, 594) has shown that fumaric acid can be produced by the action of potassium cyanide and potassium hydroxide on solid acetylene di-iodide. The same author (Abstr., 1899, i, 398) has also obtained a liquid form of acetylene di-iodide, which he regarded as the *cis*- or maleic form, whilst the solid compound was regarded as the *trans*- or fumaric isomeride.

This view has now been confirmed, and experiments are described which show conclusively that the solid iodide can be converted into fumaric acid and the liquid isomeride into maleic acid. E. G.

Nitrile of Fumaric Acid. EDWARD H. KEISER and J. J. KESSLER (*Amer. Chem. J.*, 1911, **46**, 523—528).—Keiser (Abstr., 1890, 594) and Keiser and McMaster (preceding abstract) have shown that fumaric and maleic acids can be prepared by treating the solid and liquid forms of acetylene di-iodide respectively with potassium cyanide and hydroxide. It is evident that in these syntheses the nitriles of the acids must be formed, but they could not be isolated.

Attempts have therefore been made to prepare the nitriles by heating fumaramide and ammonium maleate with phosphoric oxide. Fumaronitrile has been produced in this way, but maleonitrile could not be obtained.

Fumaramide is prepared (1) by treating ethyl bromosuccinate with dilute ammonia, and (2) by the action of 50% ammonia solution on dimethyl fumarate. When an intimate mixture of fumaramide and phosphoric oxide is heated on a sand-bath at about 120°, *fumaronitrile*, m. p. 96°, b. p. 186°/760 mm., is obtained as a sublimate of slender needles. The nitrile has a pleasant, pungent odour, sublimes readily even below 100°, and is decomposed by alkali hydroxide with formation of alkali cyanide. E. G.

Hydrogenation of Crotonaldehyde in Presence of Nickel. ROGER DOURIS (*Bull. Soc. chim.*, 1911, [iv], **9**, 922—925).—On reduction by Sabatier and Senderens' method (Abstr., 1905, i, 333), crotonaldehyde furnishes butyraldehyde and butyl alcohol with a small quantity of a syrupy substance, b. p. 115—119°/18 mm., which may contain an octyl alcohol.

n-*Butylidenediurethane*, $CHPr^{\alpha}(NH\cdot CO_2Et)_2$, m. p. 130°, obtained by condensing butyraldehyde with urethane in presence of hydrochloric acid, crystallises in rosettes of colourless needles. n-*Butyl phenylthiocarbamate*, $NHPh\cdot CS\cdot O\cdot C_4H_9$, m. p. 53°, obtained by Roschdestvensky's method (Abstr., 1910, i, 107) or by the action of phenylthiocarbimide on *n*-butyl alcohol in presence of sodium hydroxide, crystallises in long, colourless needles. T. A. H.

Ethylation of Acetone. ERNST ZERNER (*Monatsh.*, 1911, 32, 677—686).—By the action of sodamide and halogen alkyls on ketones, alkyl derivatives of these are obtained. Haller and Bauer (Abstr., 1909, i, 108) have thus prepared methyl and mixed methyl ethyl derivatives of acetone. Acetone itself yields only condensation products, particularly *iso*phorone, when treated with sodamide and ethyl bromide. Accordingly, dipropyl ketone was used as the starting point for the preparation of ethyl derivatives of acetone. In ethereal solution no action takes place, but in benzene prolonged boiling suffices to cause interaction. About half of the dipropyl ketone is recovered unchanged, and the operation has to be repeated several times. Other products are not formed in any quantity, and the ketones are separated and purified by fractional distillation. The process is repeated in order to pass to the more alkylated ketones.

The ethylacetones described do not mix with water and have a camphor-like odour; only hexaethylacetone resembles the fruity odour of dipropyl ketone. The corresponding alcohols have a sharp, peppermint-like odour.

Triethylacetone [γ-ethylheptane-δ-one], perhaps already obtained by Geuther and Frölich (Abstr., 1880, 622), has b. p. 174·5—175·5°/741 mm. On reduction it yields *triethylisopropyl alcohol* [γ-*ethylheptane-δ-ol*], which has b. p. 80—81°/10 mm. The *oxime* obtained by heating the ketone with Crismer's salt formed slender needles, m. p. 90—91°.

sym-Tetraethylacetone [γε-diethylheptane-δ-one] has b. p. 206—207·5°/771 mm. (Herzig and Zeisel, Abstr., 1894, i, 74). It does not form an oxime or phenylhydrazone. *Tetraethylisopropyl alcohol* [γε-*diethylheptane-δ-ol*], obtained on reduction, has b. p. 99—101°/13 mm.; it reacts with phenylcarbimide, forming the *phenylurethane*, m. p. 72—73°.

Pentaethylacetone [γγε-*triethylheptane-δ-one*] has b. p. 237·5—238·5°/761 mm.; *pentaethylisopropyl alcohol* [γγε-*triethylheptane-δ-ol*] has b. p. 125—127°/18 mm., and forms a *phenylurethane*, m. p. 71—72°. The mixture of the phenylurethane with that of the γε-diethylheptane-δ-ol shows a depression of 18° in the m. p.

Hexaethylacetone [γγεε-*tetraethylheptane-δ-one*] has b. p. 274—275°/759 mm., and crystallises in plates, m. p. 44°. The corresponding *hexaethylisopropyl alcohol* [γγεε-*tetraethylheptane-δ-ol*] has b. p. 159—161°/18 mm. The *phenylurethane* forms a butter-like substance, which is not characteristic. E. F. A.

An Intermediate Product of Alcoholic Fermentation. HANS VON EULER and A. FODOR (*Biochem. Zeitsch.*, 1911, 36, 401—410).—The authors fail to confirm Boyson-Jenssen's statement that dihydroxy-

ose can be isolated as an intermediate product of fermentation by yeast. They describe their method for preparing hexosephosphoric acid ester, and their results obtained with this substance agree in the main with those of Harden and Young. They have found indications that in addition to the hexosediphosphoric acid, a triosemonophosphoric acid is also formed (compare Young, Abstr., 1910, i, 12; Lebedeff, *ibid.*, 716: this vol., i, 837). S. B. S.

Decomposition of Dextrose by Dilute Sulphuric Acid. HERMANN OST and TH. BRODTKORB (*Chem. Zeit.*, 1911, 35, 1125—1126. Compare Ost and Wilkening, Abstr., 1910, i, 364).—Dextrose is converted by dilute sulphuric acid under pressure at high temperature chiefly into humin substances, formic acid, and lævulic acid; for example, about 8% of the dextrose is destroyed by heating a 5% solution of the sugar with a 2% solution of sulphuric acid for twenty-four hours at 100°, whilst 100 grams of dextrose heated with 2% sulphuric acid at 140° for seven hours yield about 16 grams of formic acid, 32 grams of lævulic acid, and 13 grams of humin substances.
W. H. G.

The Behaviour of Invert Sugar in Alkaline Solution in Presence of Hydrogen Peroxide. ADOLF JOLLES (*Biochem. Zeitsch.*, 1911, 36, 389—393).—In following the polarisation changes when invert sugar is treated with hydrogen peroxide in alkaline solutions, it is found that the rotation sinks gradually to 0°, then becomes dextrorotatory, the dextrorotation then reaches a maximum, and again decreases. The explanation of this result is that lævulose is more readily oxidised than dextrose, and is more rapidly destroyed.
S. B. S.

Mirror Image Isomerism with Chromium Compounds. I. ALFRED WERNER (*Ber.*, 1911, 44, 3132—3140).—The author has succeeded in resolving salts of the 1 : 2-dichlorodiethylenediaminechromium series into their optical isomerides, in accordance with the configurations:

These salts present a case of molecular asymmetry I, similar to that observed with the 1 : 2-dinitrodiethylenediaminecobalt salts (this vol., i, 838). Owing to the fact that the aqueous solutions of these salts are not very stable, readily giving chloro-aquo- and diaquo-salts, their resolution with silver bromocamphorsulphonate did not afford much hope of success. It was found, however, that when *d*-ammonium α-bromocamphorsulphonate was added to a freshly-prepared saturated solution of 1 : 2-dichlorodiethylenediaminechromic chloride, violet crystals of l-*dichlorodiethylenediaminechromic* d-α-*bromocamphorsulphonate* were deposited after a short time in a pure condition. From the

mother liquor, any racemate could then be precipitated as dithionate, and then, on the addition of potassium platinochloride, the [illegible] obtained as the platinochloride, from which the nitrate could be prepared by decomposition with silver nitrate. Similar results were obtained with *l*-ammonium α-bromocamphorsulphonate, d-*dichloro-diethylenediaminechromic* l-α-*bromocamphorsulphonate* being first deposited.

It is noteworthy that the *l*-dichloro-salts and *d*-bromocamphorsulphonic acid, and the *d*-dichloro-salts and *l*-bromocamphorsulphonic acid, give the least soluble salts, which is the opposite to what was observed with the cobalt salts.

The active salts are not different in colour from the inactive, but the active chlorides and dithionates are more soluble than the corresponding racemates.

The optical rotation observed are as follows (I):

	I.		II.	
	[α].	[M].	[α].	[M].
Chloride	−140°	−415·1°	−182°	[illegible]
	+140	+415·1	+184	[illegible]
Bromide	−130	−419·9	−176	[illegible]
	+124	+400·5	+168	[illegible]
Iodide	−120	−366	−164	−511
	+122	+372	+164	+511

They are much less than those of the corresponding dichlorodiethylenediaminecobalt salts (II.) (details are to be given later).

Racemisation takes place rapidly in aqueous solution, being complete at 0° after three hours in a 0·5% solution; in hydrochloric acid solution the velocity of racemisation is much slower, and at the same time the rotation of the chloride is much diminished.

Racemic 1 : 2-dichlorodiethylenediaminechromic chloride, $[Cl_2Cr\,en_2]Cl$, is best prepared as follows: Potassium chromium oxalate,

$$[Cr(C_2O_4)_3]K_3,$$

is heated with a 10% solution of ethylenediamine until a red salt begins to deposit from the dark violet solution. After cooling, the salt, which has the formula $[C_2O_4Cr\,en_2][(C_2O_4)_2Cr\,en]$, is collected, well washed with cold water, rubbed into a paste with concentrated hydrochloric acid, and kept until a portion when dried on a porous plate leaves a yellow residue of oxalatodiethylenediaminechromic chloride, $[C_2O_4Cr\,en_2]Cl$. This is collected and carefully heated with concentrated hydrochloric acid until solution is complete. The cherry-red solution so obtained is put into a crystallising dish, and alcohol added gradually, with vigorous stirring, until a violet salt begins to deposit. On keeping, a thick, violet paste of the required racemate is formed, which is well washed with alcohol and ether to remove oxalic acid, and may then be used for the resolution.

l-*Dichlorodiethylenediaminechromic* d-*bromocamphorsulphonate*,

$$[Cl_2Cr\,en_2]SO_3\cdot C_{10}H_{14}OBr,$$

forms small, shining, violet crystals, and has $[\alpha] = -35°$, $[M] = -193·55°$. The corresponding d-l-*salt* has $[\alpha]_D = +32°$, and $[M] = +176·9°$. The solutions rapidly undergo racemisation. The active 1 : 2-*dichlorodiethylenediaminechromic chlorides*, $[Cl_2Cr\,en_2]Cl,H_2O$,

...re obtained from the bromocamphorsulphonates by treatment with ...centrated hydrochloric acid; they form small, violet needles. The ...mides, $[Cl_2Cr\,en_2]Br$, were prepared from the chlorides and hydro...mic acid, and crystallise in small, reddish-violet needles. The ...rates, $[Cl_2Cr\,en_2]NO_3$, were obtained from the chlorides and nitric ...d as violet, crystalline powders. T. S. P.

Chemico-Crystallographic Examination of the Platini-chlorides, Platinibromides, Stannichlorides, and Stanni-bromides of Quaternary Ammonium Bases. A. Ries (*Zeitsch. Kryst. Min.*, 1911, 49, 513—617).—The quaternary ammonium bases, the salts of which have been examined, are those containing the groups NMe_4, NMe_3Et, NMe_3Pr^α, NMe_3Pr^β, NMe_2Et_2, $NMeEt_3$, $NMe_3{\cdot}C_4H_9$, $NMe_3{\cdot}CH_2Pr^\beta$, NMe_2EtPr^α, NEt_4, $NMe_3{\cdot}CH_2{\cdot}CHMeEt$,

$$NMe_3{\cdot}CH_2{\cdot}CH_2Pr^\beta,$$

$NMeEt_2Pr^\alpha$, $NMe_2Pr^\alpha_2$, NEt_3Pr^α, $NMeEtPr^\alpha_2$, $NMePr^\alpha_3$, $NEt_2Pr^\alpha_2$, $NEt_3{\cdot}C_5H_{11}$, $NEt_3{\cdot}CH_2Pr^\beta$, $NMeEtPr^\alpha{\cdot}CH_2Pr^\beta$, $NEtPr^\alpha_3$, NPr^α_4, $NPr^\alpha_3{\cdot}CH_2Pr^\beta$, $NMe(CH_2Pr^\beta)_3$, $NEt(CH_2Pr^\beta)_3$, $NPr^\alpha(CH_2Pr^\beta)_3$, and $N(CH_2Pr^\beta)_4$. The crystallographic properties of the platini-chlorides and -bromides, and stanni-chlorides and -bromides of these bases are described; their m. p.'s or points of decomposition are stated; in many cases the densities of the several modifications of any one salt have been determined by the floating method in acetylene tetrabromide and toluene, and the transition temperatures of the modifications have been ascertained.

After a detailed comparison of the preceding physical constants, the author states the following generalisations:

(1) The m. p.'s decrease, and the transition temperatures (of the several modifications) increase, as the molecular weights of the tetra-alkylammonium platinichlorides increase.

(2) In the case of two isomeric salts, the one containing one or more isoalkyl groups has a lower m. p. and a higher transition temperature (for corresponding modifications) than that containing normal alkyl groups.

(3) The temperatures, at which the corresponding point systems of two or more isomeric and metameric salts undergo transition into the more highly symmetric analogous point systems, are higher the less is the symmetry of the molecule corresponding with the point system.

(4) The region of stability of the different modifications is dependent on the molecular weight and the symmetry of the molecule.

Experiments on the morphotropic relations of the salts with regard to their topic axis show that the platinichloride, platinibromide, and stannichloride of a given tetra-alkylammonium base form isomorphous mixtures in all proportions.

An outstanding feature of the author's experiments is the regular shifting at high temperatures of the region of stability of the polymorphous modifications of members of homologous series. The paper concludes with a discussion of the question whether this regularity is characteristic of all salts of members of the families in the periodic table. A consideration of the transition temperatures of the modifi-

cations of the nitrates of the alkali metals, of the halides of mercury of the carbonates of the magnesium-barium group and so forth, indicates that the answer to the question is in the affirmative.

C. S.

Methylated Polypeptides. Betaine of Diglycylglycine. EMIL ABDERHALDEN and KARL KAUTZSCH (*Zeitsch. physiol. Chem.*, 1911, 75, 19—29. Compare this vol., i, 528).—*Trimethyldiglycylglycine*, $OH\cdot NMe_3\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ or

$$NH{<}{\begin{matrix}CO\cdot CH_2\cdot NMe_3{-}O\\ CH_2\cdot CO\cdot NH\cdot CH_2\end{matrix}}{>}CO,$$

obtained from chloroacetylglycylglycine and trimethylamine, is isolated in the form of the *platinichloride*, which forms orange-yellow, prismatic crystals, m. p. 181° (corr., decomp.).

The *ethyl* ester, prepared by decomposition of the platinichloride with hydrogen sulphide and treatment of the hydrogen chloride of the base with ethyl alcohol and hydrogen chloride, yields a *platinichloride*, crystallising in slender, lustrous, bright orange-yellow plates. The *platinichloride* of the corresponding *methyl* ester, prepared in the same way, crystallises in six-sided prisms, m. p. 180°. Analysis showed it to be partly hydrolytically decomposed. When prepared by dissolving the platinichloride of the base in methyl alcohol and saturating with dry hydrogen chloride, it was obtained in yellow needles, m. p. 215·5—216·5° (corr., decomp.).

Trimethyldiglycylglycine when hydrolysed with boiling concentrated hydrochloric acid for fifteen hours gives betaine hydrochloride and glycine hydrochloride, the resolution being complete. Trimethyl-*dl*-leucylglycine when boiled for two hours with fuming hydrochloric acid is recovered almost unchanged.

Hydrolysis leading to the formation of betaine took place on attempting to methylate chloroacetylalanine with trimethylamine, and a similar behaviour was shown by chloroacetyl-*l*-tyrosine. Betaine was obtained further on attempting to methylate glycylglycine with methyl iodide. When attempting to methylate polypeptides with methyl iodide and potassium hydroxide, products containing iodine and potassium were usually obtained; these probably represent potassium iodide additive products.

E. F. A.

Preparation of Iodo-fatty Acid Compounds and their Behaviour in the Animal. EMIL ABDERHALDEN and PAUL HIRSCH [and M. GUGGENHEIM] (*Zeitsch. physiol. Chem.*, 1911, 75, 38—56).—*Iodoacetylglycine*, $CH_2I\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, prepared by the reaction of glycine with iodoacetyl chloride in *N*-sodium hydroxide, sinters at 130°, and begins to melt at 142°, m. p. 160°, decomp. 165°.

dl-*a-Iodopropionylglycine*, $CHMeI\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, from glycine and a-iodopropionyl chloride, sinters and begins to melt at 60°, m. p. 80°, decomp. 135°. The *ethyl* ester crystallises in needles, which sinter at 45°, m. p. 60°, and give up iodine at 225°. dl-*a-Iodopropionyl*-dl-*alanine*, $CHMeI\cdot CO\cdot NH\cdot CHMe\cdot CO_2H$, crystallises in needles, which sinter at 155°, m. p. 180—190°, decomp. 194°. The *ethyl* ester forms yellow needles, which sinter at 50°, m. p. 52—60°, decomp. 234° with liberation of iodine.

Di-iodoelaidyl chloride, $C_{17}H_{32}I_2\cdot COCl$, is obtained as a brownish-red mass by the action of thionyl chloride on di-iodoelaidic acid. With glycine, *di-iodoelaidylglycine*, $C_{17}H_{32}I_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, is obtained. The amorphous, colourless product sinters at 52°, m. p. 57°. The ethyl ester, prepared by interaction of the chloride with glycine ester, is crystalline, m. p. 82°, after sintering at 70°.

Di-iodoelaidylalanine sinters at 54°, m. p. 64°; it has $[\alpha]_D^{20}$ − 4·9°. The corresponding ester was only obtained as a syrup.

Di-iodoelaidyl-di-iodotyrosine,

$$C_{17}H_{31}I_2\cdot CO\cdot NH\cdot CH(CH_2\cdot C_6H_2I_2\cdot OH)\cdot CO_2H,$$

sinters at 92°, m. p. 170°.

Iodobehenyl chloride, $C_{21}H_{42}I\cdot COCl$, from iodobehenic acid and thionyl chloride, could not be distilled. It couples readily with amino-acids. *Iodobehenylglycine* is an amorphous, faintly yellow-coloured, fatty mass; it sinters at 50°, m. p. 70°, decomp. 170—180°.

Ethyl di-iodobrassidate (lipoiodin), $C_8H_{17}\cdot CHI\cdot CHI\cdot C_{11}H_{22}\cdot CO_2Et$, sinters at 32°, m. p. 40°, decomp. 220—230°, liberating iodine.

The physiological experiments indicate that iodine administered as di-iodoelaidic acid is slowly but completely excreted. The iodine of di-iodoelaidylglycine was in ten days only 50% excreted. The resorption was complete, but in the case of the ethyl ester it was less complete. Most of the iodine is in the fæces; in some experiments none was present in the urine.

Di-iodo-*l*-tyrosine and di-iodoelaidyl-*l*-tyrosine are badly resorbed; ethyl di-iodobrassidate is better resorbed. E. F. A.

α-Aminobutyric Acid. EMIL ABDERHALDEN (*Zeitsch. physiol.*, 1911, **74**, 509—510).—Polemical. Koelker (this vol., i, 773) has not mentioned that Abderhalden, Chang, and Wurm (this vol., i, 526) have previously studied the behaviour of *dl*-α-aminobutyric acid towards yeast. E. F. A.

Alkylation of Commercial Cyanamide Salts. WILHELM TRAUBE and ALFRED ENGELHARDT (*Ber.*, 1911, **44**, 3149—3152. Compare Traube and Wedelstaedt, Abstr., 1900, i, 389).—The relatively pure disodium cyanamide, and likewise the crude commercial calcium cyanamide, react very readily with halogen alkyl and with dialkyl sulphate in presence of water or alcohol, forming disubstituted cyanamides. These are converted into secondary amines without difficulty, and it is easy to separate the ammonia formed at the same time. This affords a very convenient method of preparing secondary amines in quantity. Dimethyl-, diethyl-, di-*iso*amyl-, and dibenzyl cyanamide have been prepared in the manner described: from calcium cyanamide and methyl sulphate, 70—80% of the theoretical quantity of dimethylamine is obtained. Dimethylcyanamide has b. p. 163·5° (corr.); *diethylcyanamide*, b. p. 78°/16 mm.; *di-isoamylcyanamide*, b. p. 84°/14 mm.; *dibenzylcyanamide* forms transparent, rhombic plates, m. p. 53·5° (corr.). E. F. A.

Acylation and Alkylation of Cyanamide. OTTO DIELS and RICHARD GOLLMANN (*Ber.*, 1911, **44**, 3158—3165).—Cyanamide can

be acylated with ethyl chlorocarboxylate by the Schotten-Baumann method without difficulty, ethyl cyaniminodicarboxylate,

$$NC\cdot N(CO_2Et)_2,$$

being formed. With phosphoric oxide, the formation of cyanocyanate [carbimidonitrile] was expected; actually carbethoxyl isocyanate [ethyl carbimidecarboxylate], $CO:N\cdot CO_2Et$, is formed, identical with the substance prepared by Diels and Wolf (Abstr., 1906, i, 237) by the action of phosphoric oxide on ethyl nitrogen-tricarboxylate.

Ammonia converts the diacylated cyanamide into the crystalline ammonium salt of the monoacyl compound, $NC\cdot N(NH_4)\cdot CO_2Et$. Dilute acids form ethyl allophanate; concentrated acids cause the addition of water and the formation of ethyl *as*-carbamidedicarboxylate,

$$NH_2\cdot CO\cdot N(CO_2Et)_2.$$

By the interaction of methyl sulphate and cyanamide, the mono-methylcyanamide initially formed is polymerised to *isotrimethyl-melamine*, $NH<\begin{matrix}C(:NMe)\cdot NH\\C(:NMe)\cdot NH\end{matrix}>C:NMe$, but dimethylcyanamide is very readily obtained in this manner. It is easily converted into dimethylcarbamide.

Ethyl cyanoiminodicarboxylate, $NC\cdot N(CO_2Et)_2$, forms long, lustrous, silky prisms, with a burning taste, m. p. 33° (Bassler, Abstr., 1878, 214).

Methyl cyanoiminodicarboxylate, $NC\cdot N(CO_2Me)_2$, crystallises in lustrous, octahedra, m. p. 96—97°.

Ethyl carbimidecarboxylate (Diels and Wolf, *loc. cit.*) is a transparent, mobile liquid, b. p. 115—116°/781 mm.

Methyl carbimidecarboxylate, $CO:N\cdot CO_2Me$, is a transparent, mobile liquid of intensely biting odour, b. p. 97—98°; it decomposes on keeping to a colourless, crystalline compound, probably a polymeride.

Methyl phenylallophanate, $NHPh\cdot CO\cdot NH\cdot CO_2Me$, prepared by the interaction of methyl carbamidecarboxylate with aniline, crystallises in long needles, m. p. 143—144°.

The *ammonium* salt of *ethyl cyaniminocarboxylate*,

$$CN\cdot N(NH_4)\cdot CO_2Et,$$

forms lustrous, compact, octahedral crystals, m. p. 107—108°.

Ethyl as-*carbamidedicarboxylate*, $NH_2\cdot CO\cdot N(CO_2Et)_2$, crystallises in lustrous prisms, m. p. 86—87°, of faintly sweet taste. The corresponding *methyl* ester separates in slender, colourless needles, m. p. 137—138° (decomp.).

Dimethylcyanamide has b. p. 52°/14 mm.

as-*Dimethylcarbamide*, $NH_2\cdot CO\cdot NMe_2$, forms large, compact, lustrous prisms, m. p. 181—182°; it tastes sweet. E. F. A.

Synthesis of δ-Guanidinovaleric Acid. DANKWART ACKERMANN, R. ENGELAND, and FRIEDRICH KUTSCHER (*Zeitsch. Biol.*, 1911, 57, 179—182).—δ-Aminovaleric acid and cyanamide were set aside in concentrated aqueous solution for some weeks, when a crystalline crust of *δ-guanidonovaleric acid*, $CO_2H\cdot[CH_2]_4\cdot NH\cdot C(NH_2):NH$, separated. This forms short, stunted, hard crystals, m. p. 265—266°, after previously becoming brown and sintering. When evaporated

with concentrated hydrochloric acid, the *chloride* is obtained in long, lustrous needles, m. p. 170—171°. The *aurichloride* forms broad, lustrous plates, m. p. 120—122°. The *platinichloride* is very soluble and not characteristic. E. F. A.

Hypobromous [Acid and] Amides. ÉTIENNE BOISMENU (*Compt. rend.*, 1911, **153**, 678—680. Compare François, Abstr., 1909, i, 13, 491).—A description of the preparation of certain bromo-amides by the action of hypobromous acid on the amides.

Bromoformamide, H·CO·NHBr, is best prepared by the action of bromine on a solution of formamide in ethyl acetate in presence of silver oxide. It is thus obtained in crystals, m. p. 87—88° (decomp.). W. O. W.

A New Derivative of Carbamide, Chlorocarbamide. AUGUSTE BÉHAL and A. DETŒUF (*Compt. rend.*, 1911, **153**, 681—683. Compare Chattaway, Trans., 1909, **95**, 464).—Carbamide absorbs chlorine at 15°, forming a mixture of monochlorocarbamide and carbamide hydrochloride. The former may be isolated in a state of purity by adding carbamide (60 grams) to water (13 grams), cooling in ice, and passing chlorine until the weight increases by 32 grams. The clear liquid is cooled in methyl chloride for thirty minutes, the chlorocarbamide filtered in a vacuum, and washed with a previously prepared solution of the same substance.

Chlorocarbamide, NH_2·CO·NHCl, occurs in crystals, m. p. 71° (decomp.). It is soluble in five parts of water at the ordinary temperature, giving a neutral solution which slowly loses nitrogen, at the same time becoming acid and forming biuret. The substance behaves towards saturated organic compounds as a chlorinating or as an oxidising agent, or sometimes as hypochlorous acid, forming additive compounds. With unsaturated substances, it effects addition of hypochlorous acid or of chlorocarbamide, but sometimes brings about oxidation. The reactions are progressive, and their course can be followed by titration. W. O. W.

Ethyl Azodicarboxylate. OTTO DIELS and PAUL FRITZSCHE (*Ber.* 1911, **44**, 3018—3027).—Ethyl azodicarboxylate reacts normally with piperidine in cold petroleum, yielding the *dipiperidide*,

$$N_2[CO\cdot C_5NH_{10}]_2,$$

m. p. 134—135° (decomp.), golden-yellow prisms, but forms with aniline an additive *compound*, $C_{12}H_{17}O_4N_3$, m. p. 138°, of unknown constitution, although probably it is a hydrazine derivative, since it crystallises in colourless plates and prisms. A similar colourless *compound*, $C_{14}H_{21}O_4N_3$, m. p. 75—76°, is obtained with dimethylaniline.

Acting as a mild oxidising agent in consequence of its tendency to yield ethyl hydrazinedicarboxylate, ethyl azodicarboxylate very smoothly converts quinol into *p*-benzoquinone.

Reacting in methyl-alcoholic solution at 0°, hydrazine hydrate and methyl chlorocarbonate yield hydrazine hydrochloride and *methyl hydrazinecarboxylate hydrochloride*, CO_2Me·NH·NH_2,HCl, m. p. 160°.

The *base*, $C_2H_6O_2N_2$, m. p. 63°, b. p. 108°/12 mm., colourless prisms, has a faint, alkaline reaction, is volatile with steam, yields a *benzylidene* derivative, $CO_2Me\cdot NH\cdot N{:}CHPh$, m. p. 146°, and with aqueous potassium cyanate at 0°, the *semicarbazide*, $CO_2Me\cdot NH\cdot NH\cdot CO\cdot NH_2$, m. p. 169—170°, and reacts with methyl chlorocarbonate in ether to form *methyl hydrazinedicarboxylate*, $CO_2Me\cdot NH\cdot NH\cdot CO_2Me$, m. p. 131°. This ester, which is very stable and resists the attack of strong acids and bases, is also formed by the action of warm aqueous potassium hydroxide on methyl hydrazinecarboxylate hydrochloride. *Methyl azodicarboxylate*, $N_2[CO_2Me]_2$, b. p. 96°/25 mm., is prepared by the action of fuming nitric acid on methyl hydrazinedicarboxylate in nitric acid, D 1·4, at 0°, and behaves like the ethyl ester. C. S.

Dehydrogenation by Catalysis. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 3121—3125; *J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1220—1222).—Heated palladium black, prepared by reducing ammonium palladochloride by means of formic acid in presence of alkali, serves as an excellent catalyst for the dehydrogenation of *cyclo*hexane and methyl*cyclo*hexane, which lose all the six hydrogen atoms of the ring and yield hydrogen and benzene or toluene, with no trace of the tetrahydro- or dihydro-derivative of the aromatic hydrocarbon. This action commences at about 170°, and proceeds very rapidly at 200—300°.

At lower temperatures, the reverse change occurs, passage of hydrogen and benzene over the freshly-prepared palladium black heated at 100—110° resulting in the hydrogenation of the benzene. Under these conditions, the temperature of equilibrium is about 200°, since, above this temperature, in spite of the presence of excess of hydrogen, dehydrogenation occurs.

The catalytic decomposition of *cyclo*hexane hydrocarbons under the influence of palladium seems to be specific, as neither hexane, nor *cyclo*pentane, nor methyl*cyclo*pentane undergoes similar dehydrogenation, at any rate below 300°. This reaction hence serves to distinguish between five- and six-carbon atom rings. T. H. P.

Selective Catalysis: A New Tetrahydrobenzene [*cyclo*-Hexene]. NICOLAI D. ZELINSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1222—1224).—Dehydrogenation of *cyclo*hexene (prepared by the action of oxalic acid on *cyclo*hexanol) under the influence of palladium proceeds more energetically than that of *cyclo*hexane (compare preceding abstract), the products being hydrogen and benzene. The *cyclo*hexene employed in this experiment showed a continuous absorption spectrum, whilst another preparation, obtained by the action of quinoline on iodo*cyclo*hexane, was found to exhibit more or less marked selective absorption. The latter *cyclo*hexene only underwent partial dehydrogenation in presence of palladium, the benzene formed being mixed with a new *cyclo*hexene, C_6H_{10}, b. p. 77·5—78° (corr.), D_4^{20} 0·8005, n_D^{20} 1·4416, the increment of the molecular refraction being 1·58; it has a fatty, aromatic odour, and is a saturated hydrocarbon, as it reacts with neither permanganate nor bromine. T. H. P.

Isomerisation of Unsaturated Cyclic Hydrocarbons, C_8H_{12}. (Mlle.) V. I. EGOROVA (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1116—1124).—*cyclo*Hexylacetylene, $C_6H_{11}·C\vdots CH$, best prepared by the method of Darzens and Rost (Abstr., 1909, i, 899), has D_0^0 0·8602, D_0^{20} 0·8424, n_D^{20} 1·4597.

cycloHexylidene-ethylene, $CH_2:C:C_6H_{10}$, obtained on heating *cyclo*hexylacetylene with alcoholic potassium hydroxide for ten hours at 140°, is a liquid, b. p. 138—141°, D_0^0 0·8682, D_0^{20} 0·8508, n_D 1·4826, and, when heated with sodium in a sealed tube, gives the sodium derivative of *cyclo*hexylacetylene (Darzens and Rost, *loc. cit.*).

1-Vinyl-Δ¹-cyclohexene, $CH_2:CH·C\Big<\begin{matrix}CH_2·CH_2\\ CH—CH_2\end{matrix}\Big>CH_2$, prepared by heating *cyclo*hexylidene-ethylene with benzoic acid in a sealed tube for ten hours at 170°, is a liquid, b. p. 143—145°, D_0^0 0·8862, D_0^{20} 0·8701, n_D^{20} 1·49060, and, although it contains a conjugated linking, shows no optical exaltation (compare Auwers and Eisenlohr, Abstr., 1910, ii, 565); it does not react with sodium. T. H. P.

Polymerisation of Diethylene Hydrocarbons. III. Divinyl. SERGIUS V. LEBEDEFF and (Mlle.) N. A. SKAVRONSKAJA (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1124—1131).—This paper is largely a repetition of one already published (this vol., i, 26).

4-Ethenyl*cyclo*-Δ¹-hexene (*loc. cit.*) gives with bromine 1-*αβ-dibromoethyl*-3 : 4-*dibromocyclohexane*,

$$CHBr\Big<\begin{matrix}CH_2—CH_2\\ CHBr·CH_2\end{matrix}\Big>CH·CHBr·CH_2Br,$$

m. p. 69·5—70·5°. When oxidised with permanganate it yields β-carboxyadipic acid (butane-αβδ-tricarboxylic acid), m. p. 111—113° (compare Guthzeit and Engelmann, Abstr., 1902, i, 742; Leuchs and Möbis, Abstr., 1909, i, 361).

The polymeride obtained, together with the above dimeride, on heating divinyl, yields an ozonide (*loc. cit.*) identical with that given by di*cyclo*octadiene (compare Harries, Abstr., 1908, i, 254). The conclusion is hence drawn that the polymeride has the structure $\left(\begin{matrix}CH_2·CH:CH·CH_2\\ | \qquad\qquad | \\ CH_2·CH:CH·CH_2\end{matrix}\right)_x$, and is de-polymerised by the action of ozone.

T. H. P.

Benzene Problem. ERNST MOHR (*Ber.*, 1911, **44**, 2971).—Pauly has recently suggested (this vol., i, 986) that the existence of the aromatic hydrocarbon, $C_{18}H_9$, decides for the centric formula for benzene in place of the Kekulé formula. It is doubtful, however, whether this criterion can be accepted, since the hydrocarbon, $C_{18}H_9$, does not conform with the law of even numbers of atoms, and is therefore analogous to triphenylmethyl and the radicle of diphenyl nitrogen, NPh_2, rather than with benzene, naphthalene, and anthracene.

T. A. H.

A New Hypothesis on Benzene. ANÍBAL CHACÓN (Pamphlet, pp. 43).—See this vol., ii, 1080.

[Orientation in the Benzene Nucleus.] JULIUS OBERMILLER (*Ber.*, 1911, **44**, 3179—3180).—A renewed claim for priority over Holleman (compare Abstr., 1910, i, 826; also Holleman and Caland, this vol., i, 849). E. F. A.

Oxidation of Amino-acids by Alloxan, Isatin, and *p*-Benzoquinone. WILHELM TRAUBE (*Ber.*, 1911, **44**, 3145—3148).—It was first shown by Strecker that alloxan oxidises aliphatic α-amino-acids to the aldehyde of the next lower carbon series with liberation of crabon dioxide and ammonia. Hurtley and Wootton (Trans., 1911, **99**, 288) have shown that dimethylalloxan behaves similarly. It is now found that alloxan likewise oxidises anilinoacetic acid to benzaldehyde and carbon dioxide, the solution becoming red. The amount of benzaldehyde produced was determined quantitatively by means of the phenylhydrazone.

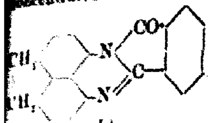
Besides alloxan, isatin, *p*-benzoquinone and toluquinone are shown to oxidise the amino-acid to aldehyde, whereas naphthaquinone and anthraquinone, parabanic acid, and chloroanil are without action. Fatty aromatic amines, for example, benzylamine, are in like manner oxidised to aldehydes by alloxan and isatin, but *p*-benzoquinone is without effect. Purely fatty amines, for example, *iso*amylamine, are not oxidised by alloxan. E. F. A.

Acenaphthene. II. FRANZ SACHS and GERHARDT MOSEBACH (*Ber.*, 1911, **44**, 2852—2862. Compare Abstr., 1910, i, 726).—The importance recently acquired by acenaphthene for technical purposes renders desirable an extension of the accurate knowledge of its substitution products. 4-Acetylaminoacenaphthene in glacial acetic acid at 0° is converted by concentrated nitric acid into *2-nitro-3-acetylaminoacenaphthene*, $NHAc\cdot C_{12}H_8\cdot NO_2$, m. p. 253°, yellow needles, in which the ortho-relation of the substituents is proved by the fact that the compound in aqueous alcohol is reduced by sodium hyposulphite to the *iminoazole*, $C_{12}H_8<^{-N}_{NH}>CMe$ (*nitrate*, $C_{14}H_{12}N_2,HNO_3$, m. p. 320°; *platinichloride*, $2C_{14}H_{12}N_2,H_2PtCl_6$; *chloride*, $C_{14}H_{12}N_2,HCl$), and also by the fact that the *2-nitro-3-aminoacenaphthene*, m. p. 222—224°, red prisms, obtained by its hydrolysis by alcohol and concentrated hydrochloric acid, is reduced by stannous chloride and hydrochloric acid to *2 : 3-acenaphthylenediamine*, m. p. 140—142°, almost colourless needles, which condenses with phenanthraquinone and with diacetyl to form the *azines*, $C_{12}H_8<^{N}_{N}>C_{14}H_8$, m. p. 293°, yellow needles, and $C_{12}H_8<^{N:CMe}_{N:CMe}$, m. p. 200°, respectively.

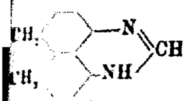
2-Nitro-3-acetylaminoacenaphthene is converted by boiling alcoholic sodium hydroxide into the *sodium* salt of 2-nitro-3-hydroxyacenaphthene, $ONa\cdot C_{12}H_8\cdot NO_2,H_2O$, dark red crystals. *2-Nitro-3-hydroxyacenaphthene* itself has m. p. 148°, crystallises in yellowish-red needles, and is reduced by sodium hyposulphite in aqueous alcohol to *2-amino-3-hydroxyacenaphthene*, m. p. 159°.

Quincke's 3 : 4-dinitroacenaphthene is obtained best by heating a

[fine]ly-divided suspension of acenaphthene in glacial acetic acid with [con]centrated nitric acid at 80° for twenty minutes. Its reduction to



(I.)



(II.)

3 : 4-acenaphthylenediamine is conveniently effected by an excess of stannous chloride and hydrochloric acid. The *peri*-position of the two amino-groups is proved by the preparation of the following substances.

Phthalo-acenaphthylene-perinone (formula I), m. p. 290°, red needles, from the diamine and phthalic anhydride at about 200°; *aceperimidine* (formula II), m. p. 285°, greenish-brown crystals, from the diamine and formic acid in boiling alcohol; *acenaphthylene-3 : 4-thiocarbamide*, $C_{12}H_8<^{NN}_{NH}>CS$, colourless crystals, from the diamine and carbon disulphide in alcohol. C. S.

Cholesterol. XIII. Cholesterylamine. ADOLF WINDAUS and [J.] ADAMLA (*Ber.*, 1911, **44**, 3051—3058).—In their attempts to prepare cholesterylamine, the authors obtained *cholesterylurethane*, $C_{27}H_{45}O\cdot CO\cdot NH_2$, m. p. 212—213°, by heating cholesterol and carbamide at 220°. *Cholesterylamine*, $C_{27}H_{45}\cdot NH_2$, m. p. 98°, is obtained by heating cholesteryl chloride and alcoholic ammonia at 180° in the presence of a little ammonium iodide. The *hydrochloride*, *sulphate*, *platinichloride*, and *picrate*, m. p. 274—275° (decomp.), are described. The *acetyl* and the *benzoyl* derivatives have m. p. 243—244° and 236° respectively. The reduction of cholestenoneoxime by sodium and boiling alcohol yields a mixture of stereoisomeric bases (*picrate*, decomp. 253°; *platinichloride*, decomp. 252°; *benzoyl* derivative, m. p. 203°). The acetylated mixture has been separated by fractionation into three individual substances; one, identical with the preceding acetyl derivative, has m. p. 243—244°, another, *β-acetylcholesterylamine*, has m. p. 216—217°, and constitutes the chief ingredient of the acetylated mixture, whilst the third, *γ-acetylcholesterylamine*, has m. p. 190°. C. S.

Synthesis of Aromatic and Hydroaromatic Alcohols Containing the Allyl Group. IPPOLYT MATSCHUREVITSCH (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 973—990).—The author has prepared a number of tertiary alcohols by the interaction of allyl bromide (or iodide), magnesium, and a carbonyl compound in ethereal solution (compare Javorsky, Abstr., 1908, i, 753).

o-4-Xylylmethylallylcarbinol, $C_6H_3Me_2\cdot CMe(OH)\cdot CH_2\cdot CH:CH_2$, prepared from *o*-4-xylyl methyl ketone, allyl bromide, and magnesium, is a colourless, viscous liquid with an aromatic odour, b. p. 144—144·5°/19·5 mm., $D_4^{21\cdot5}$ 0·97258, $n_D^{21\cdot5}$ 1·52752.

m-4-Xylylmethylallylcarbinol, prepared from *m*-4-xylyl methyl ketone, is a pleasant-smelling, colourless, viscous liquid, b. p. 139—139·5°/14·5 mm., $D_4^{21\cdot5}$ 0·97675, $n_D^{21\cdot5}$ 1·52882.

p-2-Xylylmethylallylcarbinol, prepared from *p*-2-xylyl methyl

ketone, is a liquid, b. p. 138—139°/22·5 mm., D_4^{21} 0·9771, n_D^{21} 1·52925.

1-*Allylcyclohexane*-1-*ol*, $OH\cdot C_6H_{10}\cdot CH_2\cdot CH\colon CH_2$, prepared from *cyclo*hexanone, is a liquid, b. p. 95—97°/27·5 mm., D_4^{22} 0·9348, n_D^{22} 1·47564.

1-*Methyl*-3-*allyl*-Δ^1-*cyclohexene*-3-*ol*,

$$CH_2<\begin{matrix}CMe\colon CH\\CH_2\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CH\colon CH_2,$$

prepared from 1-methyl-Δ^1-*cyclo*hexene-3-one, is a liquid, b. p. 99·5—100°/16·5 mm., D_4^{22} 0·95510, n_D^{22} 1·49923.

1 : 3-*Dimethyl*-5-*allyl*-Δ^3-*cyclohexene*-5-*ol*,

$$OH\cdot C_6H_6Me_2\cdot CH_2\cdot CH\colon CH_2,$$

prepared from 1 : 3-dimethyl-Δ^3-*cyclo*hexene-5-one, forms a fibrous, crystalline, fatty mass, m. p. 28—31°, b. p. 108—108·5°/17·5 mm.

1-*Methyl*-5-*ethyl*-3-*allyl*-Δ^1-*cyclohexene*-3-*ol*,

$$OH\cdot C_6H_6MeEt\cdot CH_2\cdot CH\colon CH_2,$$

has b. p. 120—122°/13·5 mm., D_4^{22} 0·91795, n_D^{22} 1·48731.

1-*Methyl*-5-*propyl*-Δ^1-*cyclohexene*-3-*one*, $CHPr<\begin{matrix}CH_2-CO\\CH_2\cdot CMe\end{matrix}>CH$, obtained by condensing ethyl acetoacetate and *n*-butaldehyde in presence of diethylamine to ethyl $\alpha\gamma$-diacetyl-β-propylglutarate, $CO_2Et\cdot CHAc\cdot CHPr^{\alpha}\cdot CHAc\cdot CO_2Et$, and treating the latter with alkali, is a colourless liquid, b. p. 242—244°, 128—129°/37 mm., $D_4^{22\cdot5}$ 0·9267.

1-*Methyl*-5-*propyl*-3-*allyl*-Δ^1-*cyclohexene*-3-*ol*,

$$CH_2<\begin{matrix}CMe=\!=CH\\CHPr^{\alpha}\cdot CH_2\end{matrix}>C(OH)\cdot CH_2\cdot CH\colon CH_2,$$

prepared from the preceding compound, is a crystalline, waxy mass, m. p. 34—37°, b. p. 135—136°/29 mm., $D_4^{22\cdot5}$ 0·9225.

1-*Methyl*-5-isopropyl-3-*allyl*-Δ^1-*cyclohexene*-3-*ol*, $C_{13}H_{22}O$, forms a waxy mass, m. p. 26—29°, b. p. 127—128°/25·5 mm., $D_4^{22\cdot5}$ 0·9175, $n_D^{22\cdot5}$ 1·48905.

1-*Methyl*-5-isobutyl-3-*allyl*-Δ^1-*cyclohexene*-3-*ol*, $C_{14}H_{24}O$, prepared from the corresponding hexenone, was obtained as a crystalline, waxy mass, m. p. 50—52·5°, b. p. 140—142°/38 mm. T. H. P.

Bromination of Phenol. J. G. DINWIDDIE and JOSEPH H. KASTLE (*Amer. Chem. J.*, 1911, **46**, 502—503).—It is well known that when bromine is added to an aqueous solution of phenol, tribromophenol and tribromophenol bromide are the only compounds produced. It is now shown that if bromine is added to solutions of phenol in glacial acetic acid, chloroform, carbon tetrachloride, or carbon disulphide, substitution takes place with the formation of a dibromophenol, probably the 2 : 4-derivative.

It is suggested that the peculiar behaviour of phenol in aqueous solution is due to its tendency to form quinonoid derivatives. Tribromophenol bromide, $CO<\begin{matrix}CBr\colon CH\\CBr\colon CH\end{matrix}>CBr_2$, is first produced, and reacts with phenol to form 2 : 4 : 6-tribromophenol. The mechanism of these reactions is discussed. E. G.

Isomerism and Polymorphism. II. EINAR BIILMANN (*Ber.* 1911, **44**, 3152—3157).—Polemical (compare Hantzsch, Abstr., 1910 i, 474; this vol., i, 715; Biilmann, this vol., i, 367).

Hantzsch's contention as to the persistence of the individuality of the homochromoisomerides is based on what is probably only a retention of the inoculation nuclei.

Polymorphism is a very general property. Methylcoumarinic acid has been obtained in a new modification, m. p. 86°, in addition to that, m. p. 91—92°. E. F. A.

The Reactivity of Benzene Substituents and the Acidity of Aromatic Acids in their Dependence on Orientating Influences. The Structure of Benzene. JULIUS OBERMILLER (*J. pr. Chem.*, 1911, [ii], **84**, 449—459). The author finds that the removal of the sulphoxyl group from *o*-phenolsulphonic acid by heating with hydrochloric acid at 100°, takes place more readily than with the para-compound, whilst the meta-acid, when subjected to the same treatment, remains intact.

The mobility of the sulphoxyl group thus increases as the latter approaches the hydroxyl group, as represented in Claus's diagonal formula for benzene. The view is expressed that the increase in the reactivity of the hydrogen atoms of a side-chain is coincident with an increase in its acid character. The acidity of the side-chain should accordingly be greater the less firmly it is attached, and with position-isomeric compounds increase in the order meta, para, ortho. This is confirmed by the behaviour of the sulphanilic acids and, to some extent, by the phenolsulphonic acids.

It is shown that the acidity of the hydroxyl group of the isomeric phenolsulphonic acids, as judged by the ease with which the dimagnesium salts are hydrolysed, diminishes in the order ortho, para, meta, whereas from measurements of the hydrogen ion concentration of the sodium salts the order of acidity is meta, para, ortho. This discrepancy is referred by the author to differences in the condition of the benzene ring. F. B.

Reactivity of Aromatic Bromo-compounds. II. Formation of Aromatic Disulphides of the Types R·S·R′·S·R and R·S·R′·S·R″. ÉDOUARD BOURGEOIS and A. FOUASSIN (*Bull. Soc. chim.*, 1911, [iv], **9**, 938—944. Compare Abstr., 1896, i, 17).—When *p*-dibromobenzene reacts with lead derivatives of the thiophenols, the two reactions represented by the following equations occur: (1) $2C_6H_4Br_2 + PbS_2R_2 = PbBr_2 + 2Br{\cdot}C_6H_4{\cdot}SR$, (2) $2Br{\cdot}C_6H_4{\cdot}SR + PbS_2R_2 = PbBr_2 + 2RS{\cdot}C_6H_4{\cdot}SR$. The first of these reactions takes place more rapidly than the second, and even if dibromobenzene is employed in large excess, some disulphide is always formed. The velocity of the second reaction increases with greater complexity of the thiophenol employed. Reaction begins at 180—185°, but only becomes practicable at 200°. Above 225° secondary actions occur. The two substances were heated together in an autoclave at 225°, and the resulting products extracted with ether or carbon disulphide and,

after removal of the solvent, fractionally distilled to separate the bromosulphide from the disulphide.

p-Bromodiphenyl sulphide (*loc. cit.*) reacts with the lead derivative of thiophenol to form *diphenyl* p-*phenylene disulphide*, $C_6H_4(SPh)_2$, m. p. 81·5°, b. p. 265°/14 mm., which crystallises in colourless spangles from hot alcohol.

p-*Bromophenyl* p-*tolyl sulphide*, $C_6H_4Br\cdot S\cdot C_6H_4Me$, m. p. 82·5°, b. p. 200·5°/14 mm., crystallises in pearly leaflets. *Di*-p-*tolyl* p-*phenylene disulphide*, $C_6H_4Me\cdot S\cdot C_6H_4\cdot S\cdot C_6H_4Me$, m. p. 99°, b. p. 285°/14 mm., crystallises in prismatic needles.

p-*Bromophenyl* a-*naphthyl sulphide*, m. p. 73°, b. p. 247°, forms large, prismatic needles. *Di-a-naphthyl* p-*phenylene disulphide*, m. p. 148·5°, b. p. above 360°/14 mm. (decomp.), forms colourless, rhombic tablets.

p-*Bromophenyl β-naphthyl sulphide*, m. p. 114·5°, b. p. 253°/14 mm., forms rhombic crystals. *Di-β-naphthyl* p-*phenylene disulphide*, m. p. 185°, b. p. above 360°/14 mm. (decomp.), is nearly insoluble in neutral solvents.

Phenyl p-*tolyl* p-*phenylene disulphide*, m. p. 55·5°, b. p. 272°/14 mm., obtained by heating *p*-bromodiphenyl sulphide with the lead derivative of tolyl mercaptan, is colourless and crystalline. T. A. H.

Reactivity of Aromatic Bromo-compounds. III. Action of Bromonitrobenzenes on Phenylmercaptides.

Edouard Bourgeois and P. Huber (*Bull. Soc. chim.*, 1911, [iv], 9, 944–94[illegible]).—It is known that *o*- and *p*-bromonitrobenzenes are more highly reactive than their meta-isomeride, and in confirmation of this, it is found that the two former, although they do not react with the lead derivative of thiophenol, give with the sodium derivative the corresponding nitrodiphenyl sulphides; with *m*-bromonitrobenzene, on the other hand, the nitro-group appears to undergo reduction with the formation of a red substance, m. p. 125·5°, which may be Gabriel's *m*-dibromoazobenzene (this Journ., 1877, i, 307).

4-Nitrodiphenyl sulphide, m. p. 54·4°, b. p. 240°/25 mm., or 262·5°/50 mm., or 288·2°/100 mm., forms pale yellow, prismatic needles or hexagonal tablets (Kehrmann and Bauer, Abstr., 18[illegible], i, 27), and on oxidation gives 4-nitrodiphenylsulphone (Ullmann and Pasdermadjian, Abstr., 1901, i, 383).

2-*Nitrodiphenyl sulphide*, m. p. 80·2°, forms pale orange-coloured crystals from alcohol mixed with ether. On oxidation it furnishes 2-nitrodiphenylsulphone (*loc. cit.*), which is colourless, but becomes brown on exposure to light. T. A. H.

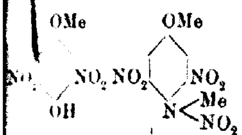
The Two Forms of Decahydro-β-naphthol (a Particular Case in Stereochemistry).

Luigi Mascarelli (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 223–227).—Leroux (Abstr., 1905, i, 27[illegible]) described decahydro-β-naphthol as having m. p. 75°, b. p. 23[illegible]. Ipatieff gave m. p. 99—100°, b. p. 242—244°. By recrystallisation of a product obtained by the latter, the author has isolated two substances, A and B, which have the same composition and molecular weight, and are both stable towards permanganate. a-*Decahydro*

naphthol forms flat, transparent crystals, m. p. 75°; b-*decahydro-naphthol* forms colourless, prismatic crystals, m. p. 103°, and is generally less soluble than its isomeride. From the consideration of the stereochemistry of monosubstituted decahydronaphthalenes it appears that four different decahydro-β-naphthols may exist, forming two pairs of enantiomorphs, and the two products above described are to be regarded as the two corresponding racemic mixtures. The stereoisomerism is due to the different positions which may be occupied by the hydrogen atoms attached to the carbon atoms 9 and 10. These two carbon atoms, although asymmetric, must necessarily have opposite configurations, and therefore the possible stereoisomerides are those due to the carbon atom to which the substituent is attached, regard being had to the different situations of the two hydrogen atoms attached to the carbon atoms 9 and 10 with which a given configuration of it can be associated. R. V. S.

Constitution of Weselsky and Benedikt's Dinitroquinol Methyl Ether. Preparation of Some Methyl Derivatives of the Dinitro-*p*-anisidines. FRÉDÉRIC REVERDIN and ARMAND DE LUC (*Arch. Sci. Phys. Nat.*, 1911, [iv], 32, 343—346; *Bull. Soc. chim.*, 1911, [iv], 9, 925—928; *J. pr. Chem.*, 1911, [ii], 84, 554—558. Compare Abstr., 1881, 1139; this vol., i, 123).—The authors have determined the constitution (I) for Weselsky and Benedikt's dinitroquinol methyl ether, and (II) for a nitroamine previously described by one of them (this vol., i, 123) with m. p. 125°.

Starting with 2 : 6-dinitro-*p*-anisidine, by the action of methyl sulphate at 100°, 2 : 6-*dinitrodimethyl-p-anisidine*, m. p. 150°, was obtained. This substance with hot nitric acid yields a *nitroamine*, m. p. 139—140°, different from their original one; thus their *nitroamine*, m. p. 125°, is that of 3 : 5-*dinitromethyl-p-anisidine* (II), and since by boiling with sodium hydroxide solution it yields Weselsky and Benedikt's ether, the latter must have the constitution (I).



(I.) (II.)

The authors were unsuccessful in attempts to methylate 3 : 5-dinitro-*p*-anisidine, but succeeded in methylating the corresponding 2 : 3- and 2 : 5-compounds, which, however, unlike the 2 : 6-compound, only yielded monomethyl derivatives.

2 : 3-*Dinitromethyl-p-anisidine* crystallises in deep red needles, m. p. 156°.

2 : 5-*Dinitromethyl-p-anisidine* crystallises in dull red, felted needles, m. p. 201—202°. W. G.

Some Derivatives of Hydroxyquinol. VI. GUIDO BARGELLINI and ERMANNO MARTEGIANI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 183—190. Compare this vol., i, 305).—The present paper deals with the products of the condensation of benzoyl chloride, anisyl chloride, and phenylacetyl chloride, respectively, with hydroxyquinol trimethyl ether in the presence of aluminium chloride.

Benzoyl chloride and hydroxyquinol trimethyl ether yield a mixture of 2 : 4 : 5-trimethoxybenzophenone and 2-hydroxy-4 : 5-dimethoxybenzophenone. 2 : 4 : 5-*Trimethoxybenzophenone*, $C_{16}H_{16}O_4$, forms pale yellow needles, m. p. 97°. Its *phenylhydrazone*, $C_{22}H_{22}O_3N_2$, crystallises in colourless scales, m. p. 178—179°, and gives a yellowish-green coloration with concentrated sulphuric acid. 2-*Hydroxy*-4 : 5-*dimethoxybenzophenone*, $C_{15}H_{14}O_4$, forms yellowish-green, flat, prismatic crystals, m. p. 106—107°. Its alcoholic solution gives a yellowish-green coloration with ferric chloride. On methylation, it yields the above trimethyl ether. The *acetyl* derivative, $C_{17}H_{16}O_5$, crystallises in slightly yellow needles, m. p. 108—110°, and dissolves in concentrated sulphuric acid, giving an orange-yellow coloration. When treated with hydrobromic acid in glacial acetic acid (compare Stoermer, Abstr., 1908, i, 190), both the trimethoxy- and the dimethoxy-derivatives yield 2 : 4-*dihydroxy*-5-*methoxybenzophenone*, $C_{14}H_{12}O_4$, which forms small, yellow needles, m. p. 183—185°, and in alcoholic solution gives a yellowish-green coloration with ferric chloride. All three methoxybenzophenones dissolve in concentrated sulphuric acid with production of an orange-yellow coloration. The positions of the methoxy- and hydroxy-groups are assigned on the basis of analogies and regularities to be found in the literature, and the constitutions of the following substances are arrived at in a similar manner.

Anisyl chloride and hydroxyquinol trimethyl ether give a mixture of 2 : 4 : 5 : 4'-tetramethoxybenzophenone and 2-hydroxy-4 : 5 : 4'-trimethoxybenzophenone. 2 : 4 : 5 : 4'-*Tetramethoxybenzophenone*,

$C_{17}H_{18}O_5$,

is a yellowish-white, crystalline powder, m. p. 122—124°, and gives an orange-yellow coloration with sulphuric acid. Its *phenylhydrazone*, $C_{23}H_{24}O_4N_2$, has m. p. 173—174°, and dissolves in concentrated sulphuric acid, with production of a green coloration. 2-*Hydroxy*-4 : 5 : 4'-*trimethoxybenzophenone*, $C_{16}H_{16}O_5$, crystallises in small, yellow needles, m. p. 127—128°, and dissolves in concentrated sulphuric acid, producing an orange coloration. The alcoholic solution gives a yellowish-green coloration with ferric chloride.

The products of the reaction between phenylacetyl chloride and hydroxyquinol trimethyl ether are 2 : 4 : 5-trimethoxy- and 2-hydroxy-4 : 5-dimethoxy-deoxybenzoin. 2 : 4 : 5-*Trimethoxydeoxybenzoin*,

$C_{17}H_{18}O_4$,

crystallises in colourless leaves, m. p. 76—77°, and gives an orange coloration when dissolved in concentrated sulphuric acid. Its *phenylhydrazone*, $C_{23}H_{24}O_3N_2$, is a yellow, crystalline powder, m. p. 142—143°; it gives a yellowish-green coloration with concentrated sulphuric acid. 2-*Hydroxy*-4 : 5-*dimethoxydeoxybenzoin*, $C_{16}H_{16}O_4$, forms colourless leaves, m. p. 94°; it dissolves in concentrated sulphuric acid with production of a yellowish-green coloration, and its alcoholic solution gives a green coloration with ferric chloride. R. V. S.

Benzyl Orthothioformate. JOHN A. SMYTHE (*Proc. Univ. Durham Phil. Soc.*, 1911, 4, 75—83. Compare Dennstedt, Abstr., 1879, 318; 1880, 646).—A white, crystalline solid, m. p. 103°, produced in small quantities when hydrogen chloride acts on benzyl mercaptan in the

...ence of glacial acetic acid, is proved to be identical with Dennstedt's ...zyl orthothioformate. Its formation is due to the presence of formic ...d as an impurity in the acetic acid employed; the yield is equivalent ...the amount of formic acid present. This indicates a ready method ...preparing the thio-ester by the action of hydrogen chloride on an ...lution of benzyl mercaptan (1 mol.) dissolved in glacial acetic acid ...ntaining sodium formate (3 mols.). The reaction under these ...ditions is reversible:

$$H\cdot CO_2H + 3CH_2Ph\cdot SH \rightleftharpoons CH(S\cdot CH_2Ph)_3 + 2H_2O.$$

The thio-ester can be accurately estimated by means of standard ...dine solution under certain conditions. The reaction takes place in ...o stages; in the first, hydrochloric acid acts as a catalyst. The ...cond stage, although reversible, proceeds almost completely, as the ...locity of reaction is very great.

$$CH(S\cdot CH_2Ph)_3 + 2H_2O \rightleftharpoons H\cdot CO_2H + 3CH_2Ph\cdot SH,$$
$$2CH_2Ph\cdot SH + I_2 \rightleftharpoons (C_6H_5\cdot CH_2)_2S_2 + 2HI.$$

W. G.

Transformations of *cyclo*Butyldiethylcarbinol. Nicolai M. ...ijner (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1149—1157).—As it ...as been found that all the transformations of *cyclo*butyldimethyl...arbinol are accompanied by isomerisation of the four-membered into ...five-membered ring, it is necessary to reconsider the transformations ...ndergone by *cyclo*butyldiethylcarbinol (compare Kijner and Amosoff, ...Abstr., 1905, i, 772). If, with the latter, the changes are similar to ...those occurring with the former, the action of oxalic acid on *cyclo*...butyldiethylcarbinol should give 1 : 2-diethyl-Δ^1-*cyclo*pentene, whilst ...the action of alcoholic potassium hydroxide on the iodo- or bromo-...derivative corresponding with the alcohol should yield 1 : 1-diethyl-Δ^2-...*cyclo*pentene. In the latter case it is, indeed, found that the resulting ...product is an unsaturated hydrocarbon, C_9H_{16}, which differs from that ...given with oxalic acid, and yields oxidation products in complete ...agreement with the conclusion that it is 1 : 1-diethyl-Δ^2-*cyclo*pentene. ...It is hence to be assumed that the action of hydrobromic (or hydriodic) ...acid on the alcohol is accompanied by isomeric change of the carbon ...ring, and so gives rise to 1 : 1-diethyl-2-bromo*cyclo*pentane.

[With W. Amosoff.]—1 : 2-*Diethyl*-Δ^1-cyclo*pentene*, $CH_2<\begin{matrix}CH_2\cdot CEt\\ \| \\ CH_2\cdot CEt\end{matrix}$, formed by the action of oxalic acid on *cyclo*butyldiethylcarbinol and previously given as $CH_2<\begin{matrix}CH_2\\CH_2\end{matrix}>C:CEt$ (*loc. cit.*), has b. p. 151·5—152°/ 774 mm., and is also obtained as a by-product in the synthesis of the carbinol itself. In the reaction with oxalic acid there is no isomeric change of the tertiary into secondary alcohol, such as occurs with *cyclo*butyldimethylcarbinol. Reduction of this hydrocarbon with concentrated sulphuric acid yields (1) a saturated hydrocarbon, C_9H_{18} (*loc. cit.*), isomeric with that obtained by reducing *cyclo*butyldiethyl...arbinol with hydriodic acid, and (2) an unsaturated *dimeride* of 1 : 2-...diethyl-Δ^1-*cyclo*pentene, $C_{18}H_{32}$, b. p. 295—300°, or 168—173°/15 mm.

The two hydrocarbons of the formula C_9H_{18} have probably structures:

$$CH_2<\begin{matrix}CH_2\cdot CHEt\\ |\\ CH_2\cdot CHEt\end{matrix} \quad\text{and}\quad CH_2<\begin{matrix}CHEt\cdot CH_2\\ |\\ CHEt\cdot CH_2\end{matrix}.$$

[With S. Voznesensky.]—1 : 1-*Diethyl*-Δ^2-*cyclopentene*,

$$CEt_2<\begin{matrix}CH{=}CH\\ |\\ CH_2\cdot CH_2\end{matrix},$$

has b. p. 143·5—144·5°/754 mm., D_0^{20} 0·8084, n_D 1·4455, and gives a green coloration with concentrated sulphuric acid and alcohol. On oxidation with permanganate, it yields an *acid*, $C_9H_{16}O_4$, which crystallises from light petroleum in needles, m. p. 85°, and forms an *anhydride*, $C_7H_{14}<\begin{matrix}CO\\ CO\end{matrix}>O$, m. p. 10—11°, D_4^{20} 1·1077, n_D 1·4689, an *anilic acid*, $CO_2H\cdot C_7H_{14}\cdot CO\cdot NHPh$, crystallising from aqueous methyl alcohol in slender needles, m. p. 142°, and an *anil*, $C_7H_{14}<\begin{matrix}CO\\ CO\end{matrix}>NPh$, separating from benzene in silky needles, m. p. 163°. On reduction with sulphuric acid, 1 : 1-diethyl-Δ^2-*cyclo*pentene gives 1 : 2-diethyl*cyclo*pentane.

2-*Bromo*-1 : 1-*diethyl*cyclo*pentane*, $C_9H_{17}Br$, has b. p. 105—106°/24 mm., D_0^{20} 1·2005, n_D 1·4895, and, on reduction with a copper-zinc couple, gives 1 : 1-*diethyl*cyclo*pentane*, $C_5H_8Et_2$, b. p. 150·5°/757 mm., D_0^{20} 0·8028, n_D 1·4388. T. H. P.

Syntheses in the Fatty Aromatic Series. II. Julius von Braun [with H. Deutsch and O. Kruber] (*Ber.*, 1911, 44, 2867—2881. Compare Abstr., 1910, i, 843).—At the present time there are, for the conversion of an alcohol into the next higher homologue, three practical methods, represented by the following schemes: (i) $R\cdot OH \longrightarrow RCl \longrightarrow R\cdot CN \longrightarrow R\cdot CO_2H \longrightarrow R\cdot CO_2Et \longrightarrow R\cdot CH_2\cdot OH$, (ii) $R\cdot OH \longrightarrow RBr \longrightarrow R\cdot MgBr \xrightarrow{(CH_2O)_3} R\cdot CH_2\cdot OH$ (iii) $R\cdot OH \longrightarrow RCl \longrightarrow R\cdot CN \longrightarrow R\cdot CH_2\cdot NH_2 \longrightarrow R\cdot CH_2\cdot NHBz \xrightarrow{PCl_5} R\cdot CH_2Cl \longrightarrow R\cdot CH_2\cdot OH$. All these methods are efficacious for the conversion of γ-chloropropylbenzene into δ-phenylbutyl alcohol, method (ii) giving the best result. For the synthesis of yet higher alcohols, however, only methods (i) and (iii) are practicable, the latter being the more convenient, since larger quantities can be manipulated at a time. In this way derivatives of phenylheptane have been prepared.

Ethyl γ-phenylbutyrate, $CH_2Ph\cdot CH_2\cdot CH_2\cdot CO_2Et$, b. p. 130—131°/10 mm., is reduced by sodium and alcohol to *δ-phenylbutyl alcohol*, $CH_2Ph\cdot[CH_2]_2\cdot CH_2\cdot OH$, b. p. 140°/14 mm., in 70% yield; the alcohol, which has a strong, unpleasant odour, forms a *phenylurethane*,

$$C_{17}H_{10}O_2N,$$

m. p. 51—52°, and is converted by concentrated hydrobromic acid at 100° into *δ-bromobutylbenzene*, b. p. 131—133°/12 mm. *ε-Phenylamyl alcohol*, $CH_2Ph\cdot[CH_2]_3\cdot CH_2\cdot OH$, b. p. 155°/20 mm., can be prepared in less than 50% yield from this bromide, magnesium, and trioxymethylene, but is obtained quantitatively by converting ε-chloroamylbenzene into *ε-phenylamyl acetate*, $CH_2Ph\cdot[CH_2]_4\cdot OAc$, b. p. 155°/12 mm., by boiling acetic acid and potassium acetate and hydro-

ing the ester by alcoholic alkali; it has an extremely pleasant, but very persistent, odour of citron.

ε-*Phenylhexonitrile*, $CH_2Ph\cdot[CH_2]_4\cdot CN$, b. p. 160—164°/13 mm., prepared from ε-iodoamylbenzene and potassium cyanide in boiling aqueous alcohol, yields by hydrolysis ε-*phenylhexoic acid*, b. p. —190°/17 mm. (*ethyl* ester, b. p. 161—163°/13 mm.), and by reduction with sodium and alcohol, ζ-*phenylhexylamine*,

$CH_2Ph\cdot[CH_2]_5\cdot NH_2$,

b. p. 144—146°/15 mm., which absorbs moisture and carbon dioxide; forms a *picrate*, m. p. 99—100°, *benzoyl* derivative, m. p. 59—61°, *platinichloride*, m. p. 216—220° (decomp.), *aurichloride*, m. p. 71—72°, and quaternary *methiodide*, $CH_2Ph\cdot[CH_2]_5\cdot NMe_3I$, m. p. 172°.

ζ-*Chlorohexylbenzene*, $CH_2Ph\cdot[CH_2]_5\cdot Cl$, b. p. 142—146°/15 mm., prepared by fusing the preceding benzoyl derivative with phosphorus pentachloride, has a pleasant odour less intense than that of ε-chloroamylbenzene, and is converted into the almost odourless ζ-*iodohexylbenzene*, b. p. 168—173°/15 mm., by sodium iodide in the usual manner. ζ-*Phenylhexyl alcohol*, b. p. 160—161°/13 mm., obtained by the reduction of ethyl ε-phenylhexoate, has a not particularly pleasant odour, less intense than that of the phenylamyl alcohol, forms an *acetate*, b. p. 166—168°/13 mm., and is converted by concentrated hydrochloric acid at 120° into the preceding chlorohexylbenzene, and by hydrobromic acid at 125° into ζ-*bromohexylbenzene*, b. p. —161°/17 mm.

ζ-*Phenylheptonitrile*, $CH_2Ph\cdot[CH_2]_5\cdot CN$, b. p. 173—178°/15 mm., obtained from iodohexylbenzene and potassium cyanide, has a very intense, persistent odour, and yields by hydrolysis ζ-*phenylheptoic acid*, b. p. 205—210°/17 mm. (*amide*, m. p. 89°), from the *ethyl* ester, b. p. —177°/16 mm., of which is obtained η-*phenylheptyl alcohol*,

$CH_2Ph\cdot[CH_2]_6\cdot OH$,

b. p. 170—172°/15 mm. This alcohol has a pleasant odour of roses, which is less intense than that of the phenylhexyl alcohol (attention is particularly called to the alternating intensity of the odour of the homologous alcohols); its *acetate* has b. p. 188—190°/24 mm. *Phenylheptylamine*, b. p. 159—160°/16 mm., obtained by the reduction of the preceding nitrile, forms a *picrate*, m. p. 120—122°, *platinichloride*, m. p. 210—213° (decomp.), *aurichloride*, m. p. 103°, and quaternary *methiodide*, $CH_2Ph\cdot[CH_2]_6\cdot NMe_3I$, m. p. 164°. By the distillation of its oily *benzoyl* derivative with phosphorus pentachloride is obtained η-*chloroheptylbenzene*, b. p. 159—164°/17 mm.; the corresponding *bromide* and *iodide* have b. p. 170—175°/15 mm. and —184°/17 mm. respectively. The iodide combines with trimethylamine to form the preceding methiodide.

β-Chloroethylbenzene is conveniently obtained by reducing benzyl cyanide with sodium and alcohol, and distilling the benzoyl derivative of the resulting β-phenylethylamine (which need not be isolated) with phosphorus pentachloride; the yield is 65—70%. C. S.

Trinaphthylmethane Compounds. ALEXEI E. TSCHITSCHIBABIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1022—1039).—Further investigation of the alcohol described by Schmidlin and Massini (Abstr.,

1909, i, 563) as tri-α-naphthylcarbinol and of the hydrocarbon regarded as tri-α-naphthylmethane, obtained by the author by reduction of the carbinol (this vol., i, 436), shows that these compounds are really α-naphthyldi-αα-naphthafluoryl alcohol (I) and α-naphthyldi-αα-naphthafluorene (II) respectively:

$$C_{10}H_7\cdot C(OH){<}\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix} \qquad\qquad C_{10}H_7\cdot CH{<}\begin{matrix}C_{10}H_6\\ |\\ C_{10}H_6\end{matrix}$$
(I.) (II.)

This stable carbinol, described by Schmidlin and Massini, is found to be formed as a result of the oxidising action of atmospheric oxygen on the unstable tri-α-naphthylcarbinol, with which it has no reactions in common, thus: $C_{31}H_{22}O + O_2 = C_{31}H_{20}O + H_2O_2$. This oxidation may also be carried out by means of neutral permanganate solution. These constitutions of the two compounds and that of the reduction product of the stable carbinol referred to above are confirmed by the previous and also by new analytical results.

Contrary to the opinion of Schmidlin and Massini, the yellow colour of the bromo-derivative (see below) of α-naphthyldi-αα-naphthafluoryl alcohol is probably due to its paraquinonoid structure,

$$(C_{10}H_7)_2{:}C{:}C{<}\begin{matrix}-C_6H_4-\\ CH{:}CH\end{matrix}{>}CHBr.$$

Also the red colour of the solution of this alcohol in sulphuric acid may be due to the formation of an oxonium compound,

$$(C_{10}H_7)_3{:}C\cdot O{<}\begin{matrix}H\\ H\\ OSO_3H\end{matrix},$$

and the blue colour obtained on heating this solution to loss of water and formation either of a carbonium salt, $(C_{10}H_7)_3{:}C\cdot OSO_3H$, or, more probably, of a complex compound of the type

$$(C_{10}H_7)_3{:}C\cdot O\cdot SO_3H,(H_2SO_4)_x.$$

Di-α-naphthyl ketone, obtained by the oxidation of di-α-naphthylcarbinol with sulphuric acid and potassium dichromate, forms large yellow prisms, m. p. 98°. In view of the higher melting point (104°) of the colourless compound obtained by Schmidlin and Massini (Abstr., 1909, i, 561), it is regarded as possible that this ketone exhibits polymorphism.

Tri-α-naphthylcarbinol, $C_{31}H_{22}O$, prepared by the interaction of di-α-naphthyl ketone and magnesium α-naphthyl bromide in presence of ether, forms compounds with both ether and benzene, the former showing the greater inclination to oxidise in the air; both these compounds dissolve with some difficulty in sulphuric acid, giving pale yellow solutions, whilst the stable carbinol dissolves readily and forms an intense red solution. The amount of the solvent in the dry benzene compound cannot be determined by analysis. The carbinol free from solvent forms drusy masses of large, colourless prisms, m. p. 140—150° (decomp.). The hydroxyl group of tri-α-naphthylcarbinol is readily replaceable by halogens; thus the action of hydriodic acid in the cold on an acetic acid solution of the carbinol gives *iodotri-α-naphthylmethane*, $CI(C_{10}H_7)_3$, which crystallises in slender, unstable, white needles, decomposing at 159°; the corresponding *bromo*-derivative forms slender, white needles, m. p. 178° (decomp.).

Naphthyldi-aa-naphthafluoryl alcohol, obtained by oxidation of -naphthylcarbinol, crystallises from acetic acid in yellow prisms, . 165°, and does not give the reaction for hydroxyl. a-Naphthyl- -naphthafluoryl bromide, $C_{31}H_{19}Br$, forms an intensely lemon- low, crystalline powder, decomposing at 215—218°, and gives a blue solution with concentrated sulphuric acid. Reduction of the mide with hydriodic acid yields a-naphthyldi-aa-naphthafluorene, p. 191°, identical with that obtained by reduction of a-naphthyldi- naphthafluoryl alcohol (compare this vol., i, 436). T. H. P.

Preparation of Cholesteryl Ethers. Otto Diels and Paul ...rzzo (*Ber.*, 1911, **44**, 2847—2851).—The following cholesteryl ...ers have been prepared by heating magnesium and cholesteryl ...oride with the corresponding alcohol; the numbers in parenthesis ...ate the temperature and time of heating. *Methyl ether*, ...H_{45}·OMe, m. p. 84° (125°, twelve hours); *ethyl ether*, $C_{27}H_{45}$·OEt, ... p. 88—90°, long needles (140°, eighteen hours); *propyl ether*, ...H_{45}·OPr, m. p. 99·5—100·5°, long prisms (140—150°, six hours); ...yl ether, m. p. 114—115° (Obermüller gives 78°) (170°, seven hours). An attempt to prepare a-cholestyl methyl ether from magnesium, cholestyl chloride, and methyl alcohol (140°, eight hours) led to the ...rmation of a *hydrocarbon*, $C_{27}H_{46}$, m. p. 56°, leaflets or prisms.

C. S.

Some Ethers of Cholesterol. Wilhelm Steinkopf and Erwin ...mmer (*J. pr. Chem.*, 1911, [ii], **84**, 460—472).—When heated ...th ethyl iodide, the potassium derivative of cholesterol yields ...hylene and cholesterol; with cholesteryl chloride it forms cholesterol ...d cholesterylene (compare Lindenmeyer, *J. pr. Chem.*, 1863, [i], ..., 321).

By heating cholesteryl chloride with zinc dust or zinc oxide, ...uthner and Suida (Abstr., 1896, i, 425) obtained a substance ...hich they considered to be cholesteryl ether. The authors have ...peated these experiments, and find that the product consists of ...olesterylene together with a small quantity of a substance, m. p. ...0—225°.

Cholesteryl phenyl ether, $C_{27}H_{45}$·OPh, obtained by heating cholesteryl ...loride with sodium phenoxide, crystallises in lustrous, silvery leaflets, ... p. 157·5°, and has, in chloroform solution, $[a]_D -34·89°$; the ...olyl ether, prepared in a similar manner, has m. p. 154·5°, $[a]_D -32·95°$ ... chloroform solution. The benzyl ether, obtained by heating the ...tassium derivative of cholesterol with benzyl chloride at 100°, forms ...all, white needles, m. p. 118·5°, $[a]_D -26·02°$ (compare preceding ...stract).

Cholesteryl p-*methylbenzyl ether*, $C_{27}H_{45}·O·CH_2·C_6H_4Me$, prepared ...om ω-bromo-*p*-xylene in a similar manner, exists in several solid ...d liquid crystalline modifications. It melts at 129—130° to a turbid, opalescent liquid, which becomes clear at 141·5°; on cooling, ...e liquid again becomes turbid, and acquires a deep violet colour, ...hich then passes successively into blue, green, red, and pink, solidi- ...ation finally taking place at 130°; in chloroform solution it has ...$]_D -26·32°$. The m-*methylbenzyl ether* melts at 93—94° to a turbid

liquid, which becomes isotropic at 125°, and shows the same colour changes as the preceding compound; in chloroform solution it has $[\alpha]_D$ − 31·76°. A microcrystallographic examination of the two last-mentioned ethers is given by Lehmann.

F. B.

***l*-Phytosterols. II.** TIMOTHÉE KLOBB (*Ann. Chim. Phys.*, 1911, [viii], 24, 410—421. Compare Abstr., 1910, i, 31; ii, 1100; 1911, i, 199).—The phytosterols of *Matricaria chamomilla*, *Tilia europea*, *Linaria vulgaris*, and *Verbascum thapsus* are described.

The oily matter left after the deposition of hydrocarbon by the acetone extract of *Matricaria chamomilla* (Abstr., 1910, ii, 1100), on treatment with potassium hydroxide in alcohol yields to ether a small amount of unsaponifiable matter, which after solution in hot alcohol deposits a mixture (m. p. 120—131°, α_D − 29·3°) of needles and hexagonal lamellæ. This mixture gives the colour reactions of the *l* phytosterols, and in addition a purple coloration with sulphuric acid containing nitrous acid. Acetic anhydride converts it into a mixture of acetyl derivatives, m. p. 150—175°, crystallising in lamellæ and flattened prisms. The mixture on bromination separates into a *substance*, $C_{36}H_{63}OAc,Br_4$, m. p. 158—160°, crystallising in hexagonal lamellæ, and a *product*, $C_{26}H_{48}OAc,Br_2$, m. p. 115—119°, which crystallises from benzene, on addition of alcohol, in microscopic granules.

[With J. GARNIER, in part.]—The unsaponifiable matter from the flowers of *Tilia europea* contains a phytosterol, $C_{27}H_{46}O$, α_D − 25·7°, m. p. 126°, crystallising in hexagonal lamellæ, and giving normal colour reactions; the *benzoyl* derivative, m. p. 140°, and the acetyl derivative, m. p. 118—119°, crystallise in hexagonal lamellæ. The second of these gives a *dibromo*-compound, $C_{26}H_{48}OAc,Br_2$, m. p. 115—120°, which separates from benzene on addition of alcohol in microscopic granules.

The phytosterol, $C_{26}H_{44}O$, obtained from *Linaria vulgaris* (Abstr., 1907, ii, 123), gives a *benzoyl* derivative, α_D − 14·55°, m. p. 147°, crystallising in nacreous, rectangular lamellæ, and an *acetyl* derivative, α_D − 38·61°, m. p. 117—130°, which crystallises simultaneously in hexagonal lamellæ and short prisms, and may be a mixture.

[With R. EHRWEIN.]—The flowers of *Verbascum thapsus* treated by the general process (Abstr., 1910, ii, 1100) furnish *verbasterol*, α_D − 3°3′, m. p. 142—144°, containing carbon 82·05% and hydrogen 11·89%, and crystallising in pearly, hexagonal lamellæ. On treatment with acetic anhydride two *substances* are formed; the *one* has m. p. 169—171°, and the *other*, m. p. 108—110°. It is impossible at present to say whether in this and the previous case the two acetyl derivatives are isomerides derived from the same phytosterol, or whether the original substance is a mixture and is resolved into its components by acetylation.

T. A. H.

3:4-Dihydroxybenzyl-methyl and -dimethyl Amines. MARC TIFFENEAU (*Bull. Soc. chim.*, 1911, [iv], 9, 928—932).—These two bases, which are closely related to adrenaline and exhibit a similar but far weaker physiological action, are described.

3:4-*Dimethoxybenzyl alcohol* (*veratryl alcohol*), D^{16} 1·180, b. p. 169°/ mm., obtained by the action of potassium hydroxide on veratraldehyde, is a viscous liquid; the *acetate*, b. p. 170—175°/13 mm., is a thick liquid; the *benzoate*, D^{0} 1·203, m. p. 36—37°, b. p. 233—236°/12 mm., crystallises on long keeping; the *phenylurethane*, m. p. 118°, is crystalline.

3:4-*Dimethoxybenzyl chloride*, m. p. 48°, is crystalline, and when heated with methylamine in a closed tube furnishes 3:4-*dimethoxybenzylmethylamine*, b. p. 135—140°/12 mm., the *hydriodide* of which has m. p. 170—171°. On demethylation, the base yields 3:4-*dihydroxybenzylmethylamine*, m. p. 179°, the *hydrochloride* of which has m. p. 182°.

When heated with dimethylamine in a closed tube, or when treated with this substance in dilute ethereal solution, 3:4-dimethoxybenzyl chloride yields 3:4-*dimethoxybenzyldimethylamine*, D^{0} 1·0578, b. p. 132—137°/12 mm., or 236—239°/760 mm., as a colourless liquid. This gives a *hydriodide*, m. p. 174°, a *methiodide*, m. p. 179°, and with acid anhydrides or chlorides furnishes the corresponding acyldimethylamines and dimethoxybenzyl esters. On demethylation of the parent base, 3:4-*dihydroxybenzyldimethylamine* is obtained, yielding a *hydrochloride*, m. p. 183°, which may also be prepared by the action of phosphorus pentachloride on 3:4-*methylenedioxybenzyldimethylamine*, D^{0} 1·101, b. p. 125°/13 mm. The latter was obtained by heating piperonyl chloride (Decker and Koch, Abstr., 1905, i, 473) with dimethylamine in a closed tube. The *hydrochloride* has m. p. 223°, the *hydriodide*, m. p. 135°, and the *methiodide*, m. p. 233°.

Piperonyl alcohol furnishes an *acetate*, m. p. 48°, and a phenylurethane, m. p. 102·5°.

T. A. H.

2:3 and 3:4-Dihydroxybenzylamines. René Douetteau (*Bull. Soc. chim.*, 1911, [iv], 9, 932—938. Compare preceding abstract).—These substances were prepared with a view to comparing their physiological action with that of adrenaline.

2:3-*Dimethoxybenzylamine*, D^{0} 1·1243, b. p. 137°/11 mm., obtained by reduction of 2:3-dimethoxybenzaldoxime (Noelting, Abstr., 1910, i, 176), is a colourless, oily liquid; the *hydrochloride*, m. p. 159°, is crystalline; the *picrate*, m. p. 205°, forms golden-yellow needles; the *methiodide* has m. p. 174°; the *acetyl* derivative, m. p. 94°, b. p. 210—211°/10 mm., is crystalline, and when treated with sodium in boiling benzene and then submitted to the action of methyl iodide furnishes 2:3-*dimethoxyphenylacetomethylamide*,

$$C_6H_3(OMe)_2\cdot CH_2\cdot NMeAc,$$

D^{0} 1·1506, b. p. 202—205°/13 mm. (approx.), as a pale yellow, viscous liquid. When heated with acetic anhydride at 150—160° this decomposes, furnishing the initial amide (compare Tiffeneau, this vol., i, 778).

2:3-*Dihydroxybenzylamine hydriodide*, m. p. 149°, obtained by the action of hydriodic acid on the dimethyl ether referred to above, is crystalline, and on treatment with silver chloride yields the *hydrochloride*, m. p. 186°; both salts give a green coloration with ferric chloride.

3 : 4-*Dimethoxybenzylamine*, b. p. 154—158°/12 mm. (approx.), prepared like its isomeride, is a colourless oil; the *hydrochloride*, m. p. 257°, the *picrate*, m. p. 169°, and the *methiodide*, m. p. 229°, were obtained crystalline. On demethylation by hydriodic acid, 3 : 4-*dihydroxybenzylamine hydriodide*, m. p. 205°, is produced, from which the *hydrochloride*, m. p. 172°, is obtained by agitation with silver chloride. T. A. H.

1-Aminocyclopentane-1-carboxylic Acid. NICOLAI D. ZELINSKI and G. STADNIKOFF (*Zeitsch. physiol. Chem.*, 1911, 75, 350—351. Compare Abstr., 1906, i, 425).—1-Aminocyclopentane-1-carboxylic acid has been obtained by the interaction of *cyclo*pentanone, ammonium chloride, and potassium cyanide in aqueous alcoholic solution, and subsequent hydrolysis of the nitrile so formed by means of hydrochloric acid. It separates from water in monoclinic crystals containing $1H_2O$, decomp. 320°. The *copper* salt was analysed. H. W.

Naphthenic Acids. I. PETROFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1198—1201).—Crude naphthenic acid from Baku naphtha was carefully purified from neutral substances and then converted into methyl esters, of which the three following were isolated: (1) b. p. 161—163°/748 mm.; the acid from this has b. p. 211—213°, which corresponds with that of Markownikoff's heptanaphthenic acid (Abstr., 1893, i, 93); (2) b. p. 169—171°/748 mm., the acid from which has b. p. 218—220°, corresponding with that of Colman and Perkin's 1-methylpentamethylene-2-carboxylate (Trans., 1888, 53, 185), and (3) $C_7H_{13}\cdot CO_2Me$, b. p. 177—178°/736 mm., D_4^0 0·945, $D_{21.7}^{21.7}$ 0·9295, $n_D^{21.7}$ 1·43005.

Reduction of ester (3) by Bouveault and Blanc's method (Abstr., 1903, i, 597) yields the *alcohol*, $C_8H_{15}\cdot OH$, as a colourless, viscous liquid with a pleasant odour, b. p. 183—184°/756 mm., or 103—104°/35 mm., D_0^0 0·8943, $D_{23.5}^{23.5}$ 0·8808, $n_D^{23.5}$ 1·44541.

The alcohol was converted through the xanthate into the naphthylene, b. p. about 108°, which contained an admixture of toluene, and hence was not analysed.

When the ester (3) was heated in a sealed tube with concentrated ammonia solution at 150°, it was converted into a mixture of two amides, which after several fractional crystallisations showed m. p. 117° and 160° respectively, but it is possible that the separation was not complete; it is probable that these two amides are *cis*- and *trans*-isomerides. Two other fractions, b. p. 192° and 200°, were also separated, and are being investigated. T. H. P.

o-Amino-p-sulphobenzoic Acid and its Derivatives, with Special Reference to their Fluorescence. II. JOSEPH H. KASTLE and R. L. HADEN (*Amer. Chem. J.*, 1911, 46, 508—518).—It has been shown in an earlier paper (this vol., i, 200) that when disilver *o*-amino-*p*-sulphobenzoate is treated with ethyl iodide, *o*-ethylamino-*p*-sulphobenzoic acid is produced. In one experiment, a small quantity of a sulphur-yellow compound was obtained, which has now been found to be diethyl *o*-ethylamino-*p*-sulphobenzoate,

$$CO_2Et\cdot C_6H_3(NHEt)\cdot SO_3Et,$$

p. 151—153° (uncorr.); it crystallises in yellow needles, and on hydrolysis is converted into o-ethylamino-p-sulphobenzoic acid.

When o-amino-p-sulphobenzoic acid (1 mol.) is heated with its silver salt (1 mol.), an acid silver salt,

$$CO_2H \cdot C_6H_3(NH_2) \cdot SO_3H, CO_2Ag \cdot C_6H_3(NH_2) \cdot SO_3Ag, 2H_2O,$$

is formed, which on being treated with ethyl iodide is converted into a mixture of diethyl o-ethylamino-p-sulphobenzoate and the original amino-acid.

Comparison has been made of the fluorescence in various solvents of o-amino-p-sulphobenzoic acid, o-ethylamino-p-sulphobenzoic acid, and the diethyl ester of the latter. The substitution of an ethyl group for a hydrogen atom of the carboxyl or amino-group has the effect of increasing the blue tint of the fluorescence; thus, in a mixture of equal volumes of water and alcohol, o-amino-p-sulphobenzoic acid shows a pinkish-purple fluorescence, and the ethylamino-acid a pure blue, whilst the diethyl ester of the latter gives a yellow solution with a pure blue fluorescence.

o-Aminoterephthalic acid exhibits a reddish-blue fluorescence in dilute aqueous and alkaline solutions, and a pure blue fluorescence in acetone solutions. Aqueous solutions of the mono- and di-ethyl esters show a pure blue fluorescence. E. G.

Isomerism of the Three *allo*-Cinnamic Acids. JULIUS MEYER (*Ber.*, 1911, **44**, 2966—2970).—Evidence is adduced in support of Biilmann's (Abstr., 1909, i, 155, 382; 1910, i, 346) view of the relationship of the three acids as opposed to Stobbe's explanation of their isomerism (this vol., i, 859).

Biilmann's observation that any one of the three acids may be obtained by inoculating the melted substance with the required acid is confirmed (Abstr., 1909, i, 155) and extended by the observation that a supersaturated solution behaves similarly. A spontaneously crystallised fusion of one form can be converted into a second form by inoculation, and the rate of this transformation descends in the following order, $42° \longrightarrow 68° > 42° \longrightarrow 58° > 58° \longrightarrow 68°$. The velocity of crystallisation is greatest for the 68° acid and least for the 42° acid. The heat developed in the change of one form into either of the other two is too small to be measured. The spontaneously crystallised fusion may consist of all three acids, and no difference in behaviour could be observed whichever form was melted in the first instance. Solutions of all three acids at the same concentration and temperature have the same electrical conductivity (compare Biilmann, Abstr., 1910, i, 346), but the solubility in water is least for the 68° acid and greatest for the 42° acid. All these observations are in harmony with Biilmann's view that the *allo*-cinnamic acids are polymorphous modifications of *cis*-cinnamic acid. T. A. H.

Transformations of *cis*-Cinnamic Acid. HUGO R. KRUYT (*Ber.*, 1911, **44**, 3108—3115. Compare Stobbe, this vol., i, 859). To explain Stobbe's results (*loc. cit.*), Tammann's theory of the mechanism of spontaneous crystallisation must be extended to the equilibrium solid–solid. The maximum rate of crystallisation occurs at a much higher temperature than that of the formation of crystalline nuclei. When a

liquid is undercooled and warmed again slightly, no crystallisation takes place at the lower temperature, but it sets in rapidly on warming owing to the marked formation of nuclei at the lower temperature. Stobbe's results are criticised in detail, and shown to be fully in agreement with this hypothesis.

E. F. A.

Compounds of 3:5-Dinitro-4-hydroxybenzoic Acid with Hydrocarbons. II. Otto Morgenstern (*Monatsh.*, 1911, 32, 711—716. Compare Abstr., 1910, i, 482).—It is sought by physical chemical measurements to establish the composition of the coloured compounds of 3 : 5-dinitro-4-hydroxybenzoic acid with aromatic hydrocarbons previously described (Abstr., 1910, i, 482). Measurements have been made of the equilibrium between hydrocarbon and acid in alcoholic solution.

If two molecules of acid combine with one of hydrocarbon $(c_1^2.c_2)/c_3$ = a constant, c_1, c_2, and c_3 being the concentrations of free acid, free hydrocarbon, and of the compound of the two respectively.

The values of c_1, c_2, and c_3 were determined experimentally in two ways. In the first a small proportion of hydrocarbon was added to the saturated solution of acid; in the second a little acid was added to the saturated hydrocarbon solution. The results show that in the second series the expression $(c_1^2.c_2)/c_3$ was not a constant, but that equilibrium was obtained between an equal number of molecules of acid and hydrocarbon, or, in other words, $(c_1.c_2)/c_3$ = a constant. The first series in which acid was in excess pointed to the formation of a compound 2 acid + hydrocarbon as assumed.

Two series of compounds are thus proved to exist in the case of phenanthrene, retene, and fluorene with dinitrohydroxybenzoic acid.

The *compound* acid + phenanthrene crystallises in yellow needles, m. p. 180° (decomp.).

The *compound* acid + fluorene is a yellowish-white powder, m. p. 210—214° (decomp.).

The analogous retene *compound* forms yellow plates, m. p. 22[illegible]° (decomp.).

E. F. A.

Studies on Tautomerism. V. Enolic Forms of Methyl Benzoylacetate and Acetylacetone. Ludwig Knorr (*Ber.*, 1911, 44, 2767—2772. Compare Meyer, this vol., i, 833).—The enolic forms of methyl benzoylacetate and acetylacetone can be isolated by the methods previously given in the case of ethyl acetoacetate (this vol., i, 516), with the difference that in these cases the enolic and not the ketonic forms crystallise out on strongly cooling solutions of the equilibrium mixtures. Methyl benzoylacetate when dissolved in a mixture of ether and light petroleum deposits at −78° acicular crystals, which can be collected, washed, and dried in the apparatus previously described. The freshly prepared substance has m. p. about 40° (bath previously heated), and gives an intense coloration with alcoholic ferric chloride solution. It has $n_D^{12 \cdot 5}$ 1·5620, whilst the equilibrium mixture has $n_D^{12 \cdot 5}$ 1·5418. These properties indicate that it is the enolic form of the ester, and, in fact, the same substance is obtained (but it is not

...pare) by treating an aqueous solution of the pure sodium salt ...below) with the calculated quantity of normal sulphuric acid at ... The production of the ketonic form takes place fairly rapidly. ...he crystals liquefy gradually even in a desiccator, and the oil attains ...the refractive index of the equilibrium mixture in the course of ...ours or days according to the name of the containing vessel.

The sodium and iron salts of the enolic ester were also prepared. The *sodium* salt, $C_{10}H_9O_3Na$, is obtained in small laminæ by mixing at 0° ... methyl-alcoholic solution of sodium methoxide with the equivalent quantity of the ester dissolved in ether. The *sodium* salt of ethyl benzoylacetate, $C_{11}H_{11}O_3Na$, is similarly prepared. The *ferric* salt of methyl benzoylacetate, $Fe(C_{10}H_9O_3)_3$, is prepared by mixing at 0° a methyl-alcoholic solution of the ester with an ethereal solution of ferric chloride, and the salt is washed with water until the chlorine reaction disappears. After recrystallisation, it forms red needles, m. p. 188° (previously sintering). From the reaction in dilute ethereal solution of molecular quantities of ferric chloride and the ester, an *iron* salt containing chlorine is obtained. It forms compact, yellow, hygroscopic crystals, which on analysis yield numbers corresponding fairly well with the formula $FeCl_2(C_{10}H_9O_3),3H_2O$. It dissolves in water and alcohol, with production of the deep reddish-violet coloration characteristic of the iron reaction.

[With HERMANN FISCHER.]—The enolic form of acetylacetone has been isolated by strongly cooling solutions of the equilibrium mixture. The crystalline substance has m. p. $-9°$, n_D^{15} 1·4609. At the ordinary temperature the substance rapidly changes into the allelotropic mixture of diketone and enol-ketone (n_D^{15} 1·4550); at 15° the transformation is complete in twenty minutes. By withdrawal of the enolic isomeride with copper hydroxide, preparations containing much of the ketonic form have also been obtained. R. V. S.

General Additive Reaction between Alkylidene-urethanes and β-Dicarboxylic Compounds. G. BIANCHI and ROBERT SCHIFF (*Gazzetta*, 1911, **41**, ii, 81—93).—When a concentrated alcoholic solution of equimolecular quantities of ethyl acetoacetate and urethane are treated with a corresponding quantity of benzaldehyde and a few drops of concentrated hydrochloric acid, the mixture becomes solid in a few minutes (formation of benzylidenediurethane), then liquefies, and finally solidifies two days later. The substance produced (compare Schiff and Bertini, Abstr., 1897, i, 493) is the additive product, *ethyl urethanobenzylacetoacetate*, $CO_2Et\cdot CHAc\cdot CHPh\cdot NH\cdot CO_2Et$, which is a white, microcrystalline powder, m. p. 96—97°. When slightly warmed with concentrated sulphuric acid, it gives a red coloration. The analogous compounds described were similarly prepared, and the reaction appears to be a general one.

Ethyl urethanobenzylbenzoylacetate,

$$CO_2Et\cdot CHBz\cdot CHPh\cdot NH\cdot CO_2Et,$$

is a white, minutely crystalline powder, m. p. 97°.

Urethanobenzylacetylacetone, $CHAc_2\cdot CHPh\cdot NH\cdot CO_2Et$, forms a white, crystalline powder, m. p. 101°; its alcoholic solution gives a red coloration with ferric chloride when warmed.

Ethyl urethanocinnamylacetoacetate,

$$CHPh{:}CH{\cdot}CH(NH{\cdot}CO_2Et){\cdot}CHAc{\cdot}CO_2Et,$$

is a white, microcrystalline powder, m. p. 92—93°.

Urethanocinnamylacetylacetone, $CHPh{:}CH{\cdot}CH(CHAc_2){\cdot}NH{\cdot}CO_2Et$, is a white, microcrystalline powder, m. p. 107°, and gives an intense red coloration with ferric chloride.

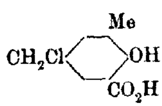
Urethanoanisylacetylacetone, $OMe{\cdot}C_6H_4{\cdot}CH(CHAc_2){\cdot}NH{\cdot}CO_2Et$, is a white, crystalline powder, m. p. 98°; with ferric chloride it gives an intense red coloration.

Urethanosalicylacetylacetone, $OH{\cdot}C_6H_4{\cdot}CH(CHAc_2){\cdot}NH{\cdot}CO_2Et$, is a white, crystalline powder, m. p. 128—130°, and gives a red coloration with ferric chloride.

All the compounds described are very stable towards mineral acids. R. V. S.

Preparation of Unsymmetrical Substituted Diphenyl-methane Derivatives. ANILINFARBEN- & EXTRAKT-FABRIKEN VORM. JOH. RUD. GEIGY (D.R.-P. 236046).—When 2-hydroxy-*m*-toluic acid is treated with chloromethyl alcohol (or analogous reagents) in the presence of fuming hydrogen chloride, condensation takes place in the para-position to the hydroxyl group.

2-Hydroxy-3-methyl-5-chloromethylbenzoic acid (annexed formula) is a colourless, crystalline powder, m. p. 197°; when heated with water it furnishes, in part, *2-hydroxy-3-methyl-5-hydroxymethylbenzoic acid*, $CO_2H{\cdot}C_6H_2Me(OH){\cdot}CH_2{\cdot}OH$, hard prisms, m. p. 186°; in part, the anhydro-compound an amorphous, colourless, insoluble, infusible powder.



2-Hydroxy-5-diethylaminobenzyl-3-methylbenzoic acid is prepared by heating 2-hydroxy-3-methyl-5-chloromethylbenzoic acid with diethylaniline, first at 70°, and subsequently at 100°; the *sodium* salt forms glistening leaflets, and the free acid crystallises in tablets, m. p. 171°.

2-Hydroxy-5-ethylaminotolylmethyl-3-methylbenzoic acid, glistening prisms, m. p. 184°, is prepared from 2-hydroxy-3-methyl-5-hydroxymethylbenzoic acid (or its anhydro-compound) and ethyl-*o*-toluidine in the presence of hydrogen chloride at 110—120°; the *sodium* salt forms glistening leaflets.

2-Hydroxy-5-methylaminobenzyl-3-methylbenzoic acid, leaflets, m. p. 193°; *2-hydroxy-5-dimethylaminobenzyl-3-methylbenzoic acid*, glistening silvery scales, m. p. 195°; *2-hydroxy-5-dimethylaminotolylmethyl-3-methylbenzoic acid*, glistening, pearly leaflets, m. p. 167°; *2-hydroxy-5-diethylaminochlorobenzyl-3-methylbenzoic acid*, prisms, m. p. 152°, and *2-hydroxy-5-diethylaminodichlorobenzyl-3-methylbenzoic acid*, needles, m. p. 230°, were also prepared. F. M. G. M.

Action of Sodium Amalgam on Naphtholcarboxylic Acids. HUGO WEIL (*Ber.*, 1911, **44**, 3058—3062).—When reduced with sodium amalgam in aqueous solution in the presence of boric acid as

...dium hydrogen sulphite, α-naphthol-2-carboxylic acid yields 1-hydroxy-2-naphthaldehyde (Bendzik and Friedländer, Abstr., 1909, i, 416).

β-Naphthol-3-carboxylic acid is reduced, under similar conditions, to tetrahydronaphthaldehyde, and β-naphthoic acid to β-naphthaldehyde, whilst α-naphthoic acid remains unchanged.

[With Walter Herdt.]—4-Sulphoxyl-α-naphthol-2-carboxylic acid is converted into 1-hydroxy-2-naphthaldehyde, the sulphoxyl group being eliminated during the reduction.

4-Bromo-α-naphthol-2-carboxylic acid, obtained by brominating α-naphthol-2-carboxylic acid in glacial acetic acid solution (compare Schmitt and Burkhard, Abstr., 1888, 59), is reduced by sodium amalgam to *4-bromo-1-hydroxy-2-naphthaldehyde*. This crystallises in yellow needles, m. p. 112°, yields a *phenylhydrazone*, m. p. 159°, and condenses with primary aromatic amines, yielding anils; the *compound*, $C_{17}H_{12}ONBr$, obtained from aniline, forms orange-yellow needles, m. p. 161°; the *compounds*, $C_{18}H_{14}ONBr$, formed by condensation with o- and p-toluidine crystallise in yellowish-red needles, m. p. 188° and 171° respectively; the *compound* from α-naphthylamine has m. p. 195°.

4-*Chloro-α-naphthol-2-carboxylic acid*, $C_{11}H_7O_3Cl$, prepared by chlorinating α-naphthol-2-carboxylic acid in glacial acetic acid solution, has m. p. 228°. It is reduced by sodium amalgam to 4-*chloro-1-hydroxy-2-naphthaldehyde*, which crystallises in yellow needles, m. p. 103°, and yields an *oxime*, m. p. 194°, and a *phenylhydrazone*, m. p. 153°; the *azine*, $C_{22}H_{14}O_2N_2Cl_2$, forms yellow needles, m. p. 179°. The aldehyde yields a *sodium* salt, crystallising in yellow leaflets, and condenses with aniline, yielding the *anil*, $C_{17}H_{12}ONCl$, which crystallises in yellow needles, m. p. 157°; with α-naphthylamine it forms the *compound*, $C_{21}H_{14}ONCl$, reddish-yellow leaflets, m. p. 188°; the *compounds*, $C_{18}H_{14}ONCl$, obtained by condensation with o- and p-toluidine are orange-yellow, and have m. p. 183° and 164° respectively. F. B.

Addition of Hydrogen Bromide to Cinnamylidenemalonic Acid, Cinnamylideneacetic Acid, and Phenylbutadiene. C. N. Riiber (*Ber.*, 1911, 44, 2974—2978).—The addition of hydrogen bromide (1 mol.) to methyl cinnamylidenemalonate (compare Hinrichsen, Abstr., 1904, i, 1012) and to methyl cinnamylideneacetate in the αβ-position (contrary to the predictions of Thiele's theory) has been proved as follows. Ethereal solutions of the respective esters are treated with hydrogen bromide; the solution of the additive compound is treated with magnesium and subsequently with water, the resulting product being finally oxidised by potassium permanganate. In both cases benzoic and succinic acids are obtained. The reaction between α-phenyl-$\Delta^{\alpha\gamma}$-butadiene and ethereal hydrogen bromide yields, in addition to a small quantity of a crystalline *substance*, $C_{10}H_9Br,2HBr$, m. p. 146°, an unstable *oil*, CHPh:CH·CHBrMe, which reacts with ethereal zinc methyl at 100° to form a *hydrocarbon*, $C_{11}H_{14}$, b. p. 84—86°/13 mm., from which benzoic and *iso*butyric acids are obtained by oxidation with potassium permanganate. C. S.

[Preparation of Derivatives of Anthraquinonecarboxylic Acids and of Anthraquinoneacridones.] BADISCHE ANILIN- & SODA-FABRIK (D.R.-P. 237236 and 237237).—Condensation products of chloro- and amino-anthraquinones have previously been described; it is now found that similar condensations take place with halogen- or nitro-anthraquinonecarboxylic acids (or bases) in the presence of condensing agents, such as aluminium chloride, sulphuric acid, or copper.

1-*Anilinoanthraquinone-2-carboxylic acid* is prepared by heating 1-nitro- or 1-chloro-anthraquinone-2-carboxylic acid with aniline at 120—130° in the presence of copper powder and anhydrous sodium acetate; it forms glistening, brown leaflets, m. p. 297—298°; the *sodium* salt, glistening, violet-black needles, gives a deep violet solution in water, and when heated at 50—60° with phosphorus pentachloride in benzene solution with aluminium chloride furnishes an *anthraquinoneacridone* as a violet-red powder.

p-*Toluidino*-1-*anthraquinone*-2-*carboxylic acid*, a violet powder, is similarly obtained with p-toluidine.

4′-*Chloro*-1-*anilinoanthraquinone*-2-*carboxylic acid*, a carmine-red powder, is furnished by the employment of p-chloroaniline.

1-*Naphthylamino*-1-*anthraquinone*-2-*carboxylic acid* is a violet powder, and the *product* from 1-chloroanthraquinone-2-carboxylic acid (2 mols.) and 4 : 4′-diaminodiphenylmethane (1 mol.), a violet-red powder, all of which furnish the corresponding *anthraquinoneacridone* on treatment with phosphorus pentachloride.

The colours of the solutions given by these substances in various solvents and other tinctorial properties are described in the original.

The second patent describes the preparation of 1-*anilinoanthraquinone-2-carboxyl chloride*, glistening, reddish-brown leaflets, by the action of phosphorus pentachloride on a benzene solution of the foregoing acid at 50—60°; this, by heating at 200° with trichlorobenzene until the evolution of hydrogen chloride ceases, yields the anthraquinoneacridone in violet-red needles.

1-*Naphthylaminoanthraquinone*-2-*carboxyl chloride*, a reddish-brown powder, is obtained by treating the corresponding acid with thionyl chloride, and on boiling with xylene furnishes the anthraquinoneacridone. F. M. G. M.

Oxidation of Phthalacene. D. MAROTTA (*Gazzetta*, 1911, 41, ii, 59—63).—The oxidation of the methyl group of phthalacene (compare Errera, Abstr., 1908, i, 183) can be effected by means of nitric acid, and 3 : 4 : 5 : 6-dibenzoylenebenzoic acid, $\begin{array}{l} C_6H_4\cdot C\text{———————}C\cdot CO \\ CO\text{—}C\cdot C(CO_2H)\text{:}CH\cdot C\cdot C_6H_4 \end{array}$, is produced. From this, on reduction, 3 : 4 : 5 : 6-dibenzylenebenzoic acid, $\begin{array}{l} C_6H_4\cdot C\text{———————}C\cdot CH_2 \\ CH_2\text{—}C\cdot C(CO_2H)\text{:}CH\cdot C\cdot C_6H_4 \end{array}$, is obtained. 3 : 4 : 5 : 6-*Dibenzoylenebenzoic acid* is prepared by heating phthalacene with dilute nitric acid (D 1·035) in a sealed tube for five hours at 200°. In this way nitration is avoided, but the reaction must be completed by opening the tube, decanting the liquid, adding more acid, and then re-heating

at 300° for five hours. The substance is an orange-red powder, m. p. 299—300°. The *potassium salt*, $C_{21}H_9O_4K,3H_2O$, can be prepared, but is very readily hydrolysable. From it the *silver* salt is obtained, and from this the *ethyl* ester, $C_{20}H_9O_2 \cdot CO_2Et$, which forms silky, yellow needles, m. p. 230°.

3 : 4 : 5 : 6-*Dibenzylenebenzoic acid* is obtained by heating the above acid with hydriodic acid and phosphorus in a sealed tube for five hours at 200°; it forms minute, pale yellow needles, m. p. above 300°. The alkali salts can be hardly isolated on account of their hydrolysability. From the *silver* salt the *ethyl* ester (brown crystals, m. p. 136—137°) was prepared. R. V. S.

Derivatives of Phthalic Acid Containing Sulphur and Nitrogen. ARNOLD REISSERT and HERMANN HOLLE (*Ber.*, 1911, **44**, 3027—3040).—Thiophthalic anhydride, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>S$, m. p. 114°, is conveniently prepared by triturating phthalic anhydride and crystallised sodium sulphide in a mortar, adding water, and pouring the mixture into dilute hydrochloric acid; the product is freed from phthalic acid by repeated extraction with aqueous sodium carbonate. It is converted into phthalide by reduction with 8% sodium amalgam.

Ethyl thiolphthalate, $CO_2Et \cdot C_6H_4 \cdot CO \cdot SEt$, b. p. about 194°/10 mm., is obtained by treating thiophthalic anhydride with cold alcoholic sodium ethoxide, and adding ethyl iodide. In a similar manner the isomeric esters, $CO_2R \cdot C_6H_4 \cdot CO \cdot SR'$ and $CO_2R' \cdot C_6H_4 \cdot CO \cdot SR$, have been prepared; thus (S)-*methyl ethyl thiolphthalate*,

$$CO_2Et \cdot C_6H_4 \cdot CO \cdot SMe,$$

b. p. 209°/16 mm., D 1·1923, is obtained by adding methyl iodide to thiophthalic anhydride in alcoholic sodium ethoxide, and yields phthalic acid, ethyl alcohol, and methyl mercaptan by hydrolysis, whilst *methyl* (S)-*ethyl thiolphthalate*, $CO_2Me \cdot C_6H_4 \cdot CO \cdot SEt$, b. p. 209°/16 mm., D 1·1906, is prepared by adding ethyl iodide to the anhydride in methyl-alcoholic sodium methoxide, and yields phthalic acid, methyl alcohol, and ethyl mercaptan by hydrolysis. When chloro-2 : 4-dinitrobenzene in methyl alcohol is added to a cold methyl-alcoholic solution of sodium methoxide and thiophthalic anhydride, and the mixture is subsequently boiled, tetranitrodiphenyl sulphide and (S)-2 : 4-*dinitrophenyl methyl thiolphthalate*, $CO_2Me \cdot C_6H_4 \cdot CO \cdot S \cdot C_6H_3(NO_2)_2$, m. p. 121°, yellow prisms, are obtained. *Methyl dithiolphthalate*, $C_6H_4(CO \cdot SMe)_2$, m. p. 124°, yellowish-brown leaflets or needles, is obtained by the addition of methyl sulphate to the liquid produced by the trituration of thiophthalic anhydride and crystallised sodium sulphide.

Thiophthalanil, $C_6H_4<\genfrac{}{}{0pt}{}{CO}{CS}>NPh$, m. p. about 144°, long, red needles, is obtained in 80% yield by heating phthalanil and phosphorus pentasulphide in boiling xylene containing a little aniline as a sulphur-carrier, and is purified best by conversion into thiophthalanilic acid by alcoholic sodium hydroxide, the acid being reconverted into the anhydride by boiling with water. The hydrolysis of thiophthalanil by *N*-sodium hydroxide and alcohol, and the subsequent oxidation of the product by potassium ferricyanide, yields *benzthiazole*-1-*o*-*benzoic acid*,

$CO_2H\cdot C_6H_4\cdot C\!\left<{S \atop N}\right>\!C_6H_4$, m. p. 189°, the *methyl* ester of which has m. p. 73°; the *hydrochloride*, $C_{14}H_9O_2NS,HCl$, and the *copper* and *calcium* salts are described, the latter yielding 1-phenylbenzthiazole by distillation.

Iminophthalanil, $C_6H_4\!\left<{CO\text{——} \atop C(:NH)}\right>\!NPh$, m. p. 170°, yellow needles, obtained from thiophthalanil and carbamide at 140—150°, dissolves in alkalis and in dilute acids, and yields *methyliminophthalanil*, $C_6H_4\!\left<{CO\text{——} \atop C(:NMe)}\right>\!NPh$, m. p. 145°, with methyl sulphate in alkaline solutions, and *benzyliminophthalanil*, m. p. 120°, with benzyl chloride and alcoholic sodium ethoxide. *Oximinophthalanil*,

$$C_6H_4\!\left<{CO\text{——} \atop C(:NOH)}\right>\!NPh,$$

m. p. 246° (decomp.), prepared from thiophthalanil, hydroxylamine sulphate, and sodium carbonate in alcoholic solution, is very stable, and has a strongly acidic, but no basic, character. The bromination of iminophthalanil in chloroform yields *bromoiminophthalbromoanil dibromide*, $C_6H_4\!\left<{CO\text{——} \atop C(:NBr_3)}\right>\!N\cdot C_6H_4Br$, brown needles, which redden at 180°, loses bromine, and yields *bromoiminophthalbromoanil*, $C_{14}H_8ON_2Br_2$, m. p. 242°, colourless leaflets. C. S.

Compounds of the Propane Series. II. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 3084—3091. Compare this vol., i, 644).—When heated at 200° and then distilled under diminished pressure, α-phthaliminoisobutyryl chloride loses carbon monoxide and hydrogen chloride, yielding *β-phthaliminopropylene*, $C_8H_4O_2{:}N\cdot CMe{:}CH_2$. This crystallises from alcohol in lustrous, hexagonal needles, m. p. 105—106°, and is hydrolysed by dilute acids to phthalic acid and acetone. It combines with bromine, forming *αβ-dibromo-β-phthaliminopropane*,

$$C_8H_4O_2{:}N\cdot CMeBr\cdot CH_2Br,$$

which forms lustrous, glassy needles, m. p. 86—89°, and, in the presence of moisture, decomposes into phthalimide and bromoacetone. When heated above its m. p. under diminished pressure, the dibromo-compound loses hydrogen bromide and yields a mixture of two isomeric *bromo-β-phthaliminopropylenes*, $C_8H_4O_2{:}N\cdot C{:}C_2H_3Br$, of which the one crystallises in leaflets or needles, m. p. 150—151°, whilst the other forms flat needles, m. p. 90—91°, with previous sintering at 86°. The interaction of bromine and *phthaliminoisobutyryl bromide* (obtained from phthaliminoisobutyric acid and phosphorus pentabromide) yields *dibromo-β-phthaliminopropylene*, $C_8H_4O_2{:}N\cdot C_3H_3Br_2$, which crystallises in lustrous needles, m. p. 169—170°; the same compound is obtained by the interaction of bromine and phthaliminoisobutyryl chloride.

Tribromo-β-phthaliminopropylene, $C_8H_4O_2{:}N\cdot C_3H_2Br_3$, obtained by the action of phosphorus and excess of bromine on phthaliminoisobutyric acid, crystallises in stout needles, resembling gypsum, m. p. 106—107°. It is hydrolysed by potassium hydroxide in aqueous alcoholic solution to a *dibasic acid*, $C_{11}H_9O_5N$. This crystallises in small needles, which become brown at 135° and decompose at

141—144°; the *silver salt*, $C_{11}H_7O_5NAg_2,1\frac{1}{2}H_2O$, and *barium salt*, $C_{11}H_7O_5NBa,3H_2O$, are described.

It is suggested that the above-mentioned tribromo-compound has the constitution $C_6H_4O_2\colon N\cdot C(CHBr_2)\colon CHBr$ or

$$C_6H_4O_2\colon N\cdot C(CH_2Br)\colon CBr_2,$$

whilst the dibasic acid has probably the formula

$$CO_2H\cdot C_6H_4\cdot CO\cdot NH(CO_2H)\colon CH_2.$$

When phthaliminocyclopropane (*loc. cit.*) is heated with excess of bromine on the water-bath, it yields a *tribromo*-derivative, $C_{11}H_8O_2NBr_3$, which crystallises in colourless needles, m. p. 162—163°, with previous softening at 159°, and is isomeric with the above tribromo-β-phthaliminopropylene.

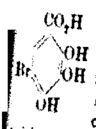
F. B.

Preparation of 2 : 4-Diamino*iso*phthalic Acid and Derivatives. MARSTON TAYLOR BOGERT (D.R.-P. 236848).—Diacetyl-*m*-xylylene-4 : 6-diamine, m. p. 295° (compare Morgan, Trans., 1902, 81, 93), when oxidised with potassium permanganate in the presence of magnesium sulphate yields 4 : 6-*diacetylaminoisophthalic acid*, colourless needles, m. p. 276°, which on hydrolysis with concentrated hydrochloric acid furnishes 4 : 6-*diaminoisophthalic acid hydrochloride* as yellow needles; the free *acid* is a colourless powder, m. p. 235° (decomp.); the *bisacetylanthranil* of the acid is crystalline, m. p. 283°, and forms with aniline (2 mols.) a condensation *product*, colourless needles, m. p. 315°.

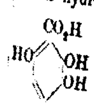
F. M. G. M.

Trihydroxybenzoic Acids. FRANZ VON HEMMELMAYR (*Monatsh.*, 1911, 32, 773—791).—The influence of the position of the hydroxyl groups on the entry of bromine, and on the chemical behaviour of the substitution compounds obtained, has been studied in the case of the trihydroxybenzoic acids.

Phloroglucinolcarboxylic acid does not form a substitution compound, but on treatment with bromine, carbon dioxide is eliminated, and ultimately di- or tri-bromophloroglucinol is formed.



Pyrogallolcarboxylic acid forms a monobromo-derivative, which in view of the fact that it can be esterified, is considered to have the annexed constitution. Further treatment with bromine causes the elimination of carbon dioxide and subsequent formation of di- or tri-bromopyrogallol. The former is probably identical with a substance described by Einhorn (Abstr., 1904, i, 238).



The hydroxyquinolcarboxylic acid described by Thiele and Jäger (Abstr., 1901, i, 701) cannot be esterified by alcohol and hydrogen chloride. Accordingly, the annexed constitutional formula is the most probable. Only one bromine atom could be introduced, further action again causing elimination of the carboxylic group and formation of a dibromohydroxyquinol. The monobromo-compound could not be esterified.

The rate of elimination of carbon dioxide on boiling with water has been determined for each of these compounds; in general, the entry of the bromine atom doubles the rate of decomposition.

Dibromophloroglucinol forms colourless, lustrous needles, m. p. 171—172°; it dissolves in sodium carbonate or in ammonia with an orange-yellow coloration. *Dibromophloroglucinyl triacetate* forms colourless needles, m. p. 128—129°.

Monobromopyrogallolcarboxylic acid forms colourless or slightly yellow needles, which on heating sinter, decomp. 230°. The barium salt forms crystalline plates; the methyl ester separates in colourless needles, m. p. 135°. *Dibromopyrogallol* forms bunches of brown needles, which sinter at 160°, decomp. 173°. *Tribromopyrogallol* forms yellowish-brown plates, decomp. 180—186°.

The *barium* salt of hydroxyquinolcarboxylic acid separates in brown crystals. *Monobromohydroxyquinolcarboxylic acid* forms feather-like groups of needles, decomp. 199°. *Dibromohydroxyquinol* forms large, colourless, prismatic crystals. E. F. A.

Preparation of Tribasic Phenolphthalates. PHILIP A. KOBER and J. THEODORE MARSHALL (*J. Amer. Chem. Soc.*, 1911, **33**, 1779—1785). —In an earlier paper (this vol., i, 300), tripotassium phenolphthalate was described. An account is now given of the preparation of this salt and the corresponding trisodium salt,

$$\begin{matrix}CO_2Na\cdot C_6H_4\\ ONa\cdot C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_4\cdot ONa\\ OH\end{matrix},6H_2O,$$

which crystallises in rhombohedra, and is more soluble, but less stable, than the potassium salt. Of the three alkali atoms in these salts, two are readily displaced by the action of weak acids, such as acetic and carbonic acids, whilst the third, probably that attached to the carboxyl group, is more resistant, but is easily displaced by mineral acids. E. G.

Unsaturated δ-Ketonic Acids. ELMER P. KOHLER (*Amer. Chem. J.*, 1911, **46**, 474—502).—Unsaturated δ-lactonic acids have not been prepared for the first time. They can be readily obtained by the methods used for preparing the corresponding saturated compounds, or by introducing bromine into saturated ketonic acids and eliminating hydrogen bromide from the product.

Methyl γ-benzoyl-β-phenylethylmalonate can be obtained in good yield by the condensation of methyl malonate with phenyl styryl ketone in presence of piperidine; on hydrolysis, it yields the free acid. The *ethyl* ester, $CH_2Bz\cdot CHPh\cdot CH(CO_2Et)_2$, m. p. 65°, forms friable needles, and, on bromination, yields two stereoisomeric ethyl γ-bromo-γ-benzoyl-β-phenylethylmalonates, m. p. 88° and 43°, the former crystallising in needles and the latter in large prisms or tablets. The methyl ester similarly yields two *bromo*-derivatives, m. p. 113° and 87°, crystallising in needles and prisms respectively; on the addition of bromine to solutions of these compounds in carbon tetrachloride, two isomeric *methyl αγ-dibromo-γ-benzoyl-β-phenylethylmalonates*, m. p. 132° and 94°, are produced, which crystallise in needles and large tablets respectively.

Methyl γ-benzoyl-β-phenylvinylmalonate, $CHBz:CPh\cdot CH(CO_2Me)_2$, m. p. 94°, obtained by the action of potassium hydroxide on the methyl γ-bromo-γ-benzoyl-β-phenylethylmalonates, forms large, trans-

...rent prisms or tablets; it does not combine with bromine, but yields ...bromo-derivative, m. p. 141°, which crystallises in prisms or tablets. When methyl γ-benzoyl-β-phenylvinylmalonate is hydrolysed with ...ssium hydroxide, *mono-* and *di-potassium* salts are produced, which ...treatment with acids yield *γ-benzoyl-β-phenylbutyrolactonic acid*, $\underset{\text{O——CO}}{CH_2Bz\cdot CPh\cdot CH\cdot CO_2H}$, which crystallises from water in small, lustrous ...ramids containing $2H_2O$. When heated the hydrated acid melts ...about 100°, then loses water, re-solidifies, and finally melts and ...composes at about 170°. The product of hydrolysis of the unsaturated ...ster contains also a small quantity of *δ-hydroxy-βδ-diphenylcrotolactonic acid*, $\underset{\text{O—CO—CH}\cdot CO_2H}{OH\cdot CPh\cdot CH{:}CPh}$, m. p. about 170°, which ...rystallises in slender needles. When this acid is heated above its ...m. p., it is converted into benzoylphenylvinylacetic acid and *...hydroxy-βδ-diphenyl-δ-crotolactone*, $\underset{\text{O————CO}}{OH\cdot CPh\cdot CH{:}CPh\cdot CH_2}$, m. p. 24...

When benzoylphenylbutyrolactonic acid is heated at 170—185° ...until carbon dioxide ceases to be evolved, four substances are pro...duced, namely: (1) γ-benzoyl-β-phenylvinylacetic acid; (2) an *acid*, m. p. 180°, isomeric with γ-benzoyl-β-phenylvinylacetic acid, and ...crystallising in large plates; (3) γ-benzoyl-β-phenyl-β-butyrolactone, ...and (4) a small quantity of an unsaturated *lactone*, probably $\underset{\text{CH—CO—O}}{Ph\cdot CH{:}CPh}$, m. p. 172°, which forms thin, lemon-yellow plates.

γ-Benzoyl-β-phenylvinylacetic acid, $CHBz{:}CPh\cdot CH_2\cdot CO_2H$, m. p. 135°, ...forms small, colourless prisms. When a solution of this acid in ...methyl alcohol is saturated with hydrogen chloride, *methyl β-chloro-...benzoyl-β-phenylbutyrate*, $CH_2Bz\cdot CPhCl\cdot CH_2\cdot CO_2Me$, m. p. 131°, is ...produced, which crystallises in slender needles. The unsaturated acid ...combines with bromine to form two stereoisomeric *βγ-dibromo-γ-benz...oyl-β-phenylbutyric acids*, $CHBzBr\cdot CPhBr\cdot CH_2\cdot CO_2H$, which decom...pose without melting; one form crystallises in plates and the other in ...slender needles. When these dibromides are added to solution of ...sodium hydrogen carbonate, they are converted into a *lactone*, probably $\underset{\text{——————CO}}{CHBz\cdot CPh{:}CH}$, m. p. 131°, which forms pale yellow needles.

γ-Benzoyl-β-phenyl-β-butyrolactone, $\underset{\text{O——CO}}{CH_2Bz\cdot CPh\cdot CH_2}$, m. p. 93°, ...crystallises in needles or prisms, and is very stable; it is not affected ...when boiled with water or sodium carbonate solution, and does not ...decompose when heated at 200°. When the lactone is added to ...alcoholic potassium hydroxide, it is converted into γ-benzoyl-β-phenyl...vinylacetic acid, and if treated with methyl alcohol and hydrogen ...chloride, it is transformed into methyl β-chloro-γ-benzoyl-β-phenyl...butyrate. If a solution of the lactone in glacial acetic acid is ...saturated with hydrogen bromide, *β-bromo-γ-benzoyl-β-phenylbutyric acid*, $CH_2Bz\cdot CPhBr\cdot CH_2\cdot CO_2H$, is produced, which forms long needles

and decomposes without melting. When an ethereal solution of γ-benzoyl-β-phenyl-β-butyrolactone is treated with magnesium ethyl bromide and the product is decomposed with water before the addition of acid, *δ-hydroxy-ββ-diphenyl-β-heptolactone*,

$$\mathrm{OH{\cdot}CPhEt{\cdot}CH_2{\cdot}\underset{\displaystyle O\text{———}}{C}Ph{\cdot}\underset{\displaystyle CO}{C}H_2},$$

m. p. 190°, is produced, but if the magnesium derivative is poured directly into a mixture of ice and hydrochloric acid, a *stereoisomeride*, m. p. 140°, is formed. On adding acids to solutions of the potassium salts of these lactones, a third *isomeride*, m. p. 150°, is obtained, which must be a δ-lactone.

γ-Bromo-γ-benzoyl-β-phenylbutyric acid, $\mathrm{CHBzBr{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H}$, was obtained in two stereoisomeric forms by the action of bromine on benzoylphenylbutyric acid, one, m. p. about 189° (decomp.), which forms flat needles or plates, and the other, m. p. 145° (decomp.), which crystallises in small prisms; the corresponding *methyl* esters have m. p. 132° and 87° respectively. When these bromo-acids are dissolved in a solution of sodium carbonate, each is converted into a mixture of two stereoisomeric *γ-benzoyl-β-phenyl-γ-butyrolactones*,

$$\mathrm{\underset{\displaystyle O\text{————————}}{C}HBz{\cdot}CHPh{\cdot}\underset{\displaystyle CO}{C}H_2},$$

one, m. p. 130°, forming large tablets, and the other, m. p. 98°, lustrous needles. *γ-Hydroxy-γ-benzoyl-β-phenylbutyric acid*,

$$\mathrm{OH{\cdot}CHBz{\cdot}CHPh{\cdot}CH_2{\cdot}CO_2H},$$

m. p. 160° (decomp.), obtained when either of the lactones is dissolved in alcoholic potassium hydroxide and subsequently acidified, forms long, colourless needles. By the action of magnesium ethyl bromide on the lactone of m. p. 130°, *γ-hydroxy-γ-benzoyl-β-phenyl-γ-heptolactone*,

$$\mathrm{OH{\cdot}CPhEt{\cdot}\underset{\displaystyle O\text{————————}}{C}H{\cdot}CHPh{\cdot}\underset{\displaystyle CO}{C}H_2},$$

m. p. 103°, is produced, which crystallises in needles.

E. G.

peri-Naphthalideacetic Acid. HERMANN PAULY [with WILHELM WALTER] (*Ber.*, 1911, 44, 2785—2786. Compare Sachs and Brigl, this vol., i, 719).—This substance, $\mathrm{C_{10}H_6{<}^{O}_{CO}{>}CH{\cdot}CH_2{\cdot}CO_2H}$, was prepared by oxidation of naphthalidedimethyl ketone (Zink, Abstr., 1902, i, 159) with sodium hypobromite. It crystallises in rosettes of needles, m. p. 168·5° (bath previously heated), 158° (bath not previously heated). The *silver* salt, $\mathrm{C_{14}H_9O_4Ag}$, forms microscopic laminæ.

R. V. S.

Preparation of Acyl Derivatives of o-Salicyloxybenzoic Acids. C. F. BOEHRINGER & SÖHNE (D.R.-P. 236196 and 237211).—When *o*-salicyloxybenzoic acid is treated with condensing agents (such as acetic anhydride), acyl derivatives of general formula

$$\mathrm{R{\cdot}O{\cdot}C_6H_4{\cdot}CO{\cdot}O{\cdot}C_6H_4{\cdot}CO_2H}$$

(R = an acyl group) are obtained, and the acetyl and ethylcarbonyl derivatives (Abstr., 1910, i, 386) have now been prepared by the

...ion of acetic anhydride and ethylchlorocarbonate respectively on ...cyloxybenzoic acid.

Benzoyloxy-o-benzoyloxybenzoic acid, leaflets, m. p. 153°, was ...ined by the action of benzoyl chloride on *o*-salicyloxybenzoic acid ...aqueous alkaline solution, and *o-salicyloxybenzoyl carbonate*,

$$C_{29}H_{18}O_{11},$$

...p. 192°, in a similar manner with carbonyl chloride.

The second patent states that the preparation of *o*-acyloxybenzoyloxy...zoic acids proceeds smoothly without the application of heat if the ...uired *o*-acyloxybenzoic acid is left in contact with a tertiary amine dur... a long period. A solution of acetyloxybenzoic acid in pyridine was ...nd after some days to contain *o*-acetyloxybenzoyloxybenzoic acid, ...d a dimethylaniline solution of ethylcarbonylsalicylic acid furnished ...thylcarbonyloxybenzoyloxybenzoic acid. F. M. G. M.

Angeli-Rimini Reaction of the Aldehydes. LUIGI BALBIANO (...ti R. Accad. Lincei, 1911, [v], 20, ii, 245—249. Compare Paolini, ... vol., i, 779; Tiffeneau, Abstr., 1910, i, 379).—The author now ...ds that the above reaction is given also by anisylacetone and other ...ones, so that he no longer maintains the opinion that the substance ...ained by the dehydration of anethole glycol is an aldehyde.

R. V. S.

[Solutions of Benzaldehyde and Hydrogen Cyanide in ...ater.] LEOPOLD ROSENTHALER (*Arch. Pharm.*, 1911, 249, 510—511. ...mpare Abstr., 1909, i, 623).—A reply to Wirth, this vol., i, 875.

T. A. H.

Preparation of *o*-Nitrobenzaldehyde. SOCIÉTÉ CHIMIQUE DES ...SINES DU RHÔNE (D.R.-P. 237358).—When dilute aqueous solutions ... salts of *o*-ω-dinitrotoluene are treated at a low temperature with ...assium permanganate, they yield *o*-nitrobenzaldehyde according ...the equation:

$$3NO_2\cdot C_6H_4\cdot CH:NO_2Na + 2KMnO_4 + H_2O =$$
$$3NO_2\cdot C_6H_4\cdot CHO + 3NaNO_2 + 2MnO_2 + 2KOH.$$

...If the mixture is kept neutral or only slightly alkaline, a theoretical ...ld of pure *o*-nitrobenzaldehyde is produced. F. M. G. M.

Oxidation of *m*-Nitrobenzoylformaldehyde. WILLIAM L. EVANS ... EDGAR JOHN WITZEMANN (*J. Amer. Chem. Soc.*, 1911, 33, ...2—1779).—In an earlier paper (Abstr., 1908, i, 338) an account ... been given of the behaviour of *m*-nitrobenzoylcarbinol towards ...dising agents. The work has now been extended to the preparation ... oxidation of *m*-nitrobenzoylformaldehyde.

The *osazone* of *m*-nitrobenzoylformaldehyde, m. p. 223°, forms dark ... needles.

When the aldehyde is treated with potassium permanganate in ...tral or alkaline solution, or with potassium ferricyanide, freshly ...cipitated silver oxide, or freshly precipitated mercuric oxide in ...sence of sodium hydroxide in each case, *m*-nitrobenzoic acid is ... sole product of oxidation. In the absence of alkali hydroxide,

freshly precipitated silver oxide and mercuric oxide do not effect the oxidation of the compound at the ordinary temperature, but at high convert it into *m*-nitrobenzoic acid. When the aldehyde is treated with hot solutions of copper acetate or with alkali hydroxides, it is transformed into *m*-nitromandelic acid.

The results of these experiments and those recorded in the earlier paper (*loc. cit.*) indicate that *m*-nitrobenzoylcarbinol and *m*-nitrobenzoylformaldehyde behave similarly to the parent substances (compare Evans, Abstr., 1906, i, 269), but that they are more sensitive to reagents in the presence of alkali hydroxides. Moreover, the nitro-derivatives show a greater tendency to progress to the benzoic acid stage, yielding *m*-nitrobenzoic acid, than to give the possible intermediate compounds, namely, *m*-nitromandelic and *m*-nitrophenylglyoxylic acids.

E. G.

Catalytic Conversion of 1-Methyl*cyclo*pentane-3-one into Methyl*cyclo*pentane. NICOLAI D. ZELINSKY (*Ber.*, 1911, 44, 2781—2782).—Skita and Ritter (this vol., i, 272) have shown that the catalytic reduction of a number of substances containing six-membered rings is attended by the production of small quantities of the corresponding saturated cyclic hydrocarbons. The author finds that catalytic reduction of 1-methyl*cyclo*pentane-3-one with nickel at 150—160° yields a mixture of water, the alcohol, the ketone, and the hydrocarbon, whilst if the temperature is raised to 250°, methyl*cyclo*pentane is obtained in good yield. The fact that at this temperature no dehydrogenisation occurs marks the difference between the five-membered and the six-membered ring.

R. V. S.

Catalytic Reduction in a Vacuum. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2779—2780).—Reductions by means of hydrogen in the presence of nickel can be accomplished under reduced pressure. From 1 : 3-dimethyl-Δ^3-*cyclo*hexene-5-one at 200° and 75—80 mm., 1 : 3-dimethyl*cyclo*hexanone was obtained. From *iso*phorone at a pressure of 70—75 mm., the temperature of the nickel being 180°, dihydro*iso*phorone was produced.

R. V. S.

Synthesis of New Hydroaromatic Ketones. GEORGES DARZENS and H. ROST (*Compt. rend.*, 1911, **153**, 772—775. Compare Abstr., 1910, i, 856; 1907, i, 627).—A description of new ketones obtained by the action of an organomagnesium halides on acid chlorides at −10°. The products are purified from small quantities of tertiary alcohols through the agency of their semicarbazones.

cyclo*Hexoyl*cyclo*hexene*, $C_6H_{11}\cdot CO\cdot C_6H_9$, b. p. 136°/19 mm., forms a *semicarbazone*, m. p. 117—118°. n-*Butyryl*cyclo*hexane*,

$$C_6H_{11}\cdot CO\cdot C_3H_7,$$

b. p. 94°/13 mm., forms a *semicarbazone*, m. p. 153—154°.

The following acid chlorides were obtained by the action of thionyl chloride on the acids: cyclo*Hexeneacetyl chloride*, $C_6H_{11}\cdot CH_2\cdot COCl$, b. p. 98—100°/23 mm.; 2-*methyl*cyclo*hexeneacetyl chloride*, b. p. 104—105°/13 mm.; 3-*methyl*cyclo*hexeneacetyl chloride*, b. p. 95—96°/11 mm.; 4-*methyl*cyclo*hexeneacetyl chloride*, b. p. 109—110°/8 mm.; 4-*methyl*cyclo*hexylacetyl chloride*, b. p. 75°/7 mm.

1-Methyl-4-tert.-butylcyclohexanone (this vol., i, 290) condenses with ethyl chloroacetate, giving *ethyl hydroxy-1-methyl-4-tert.-butylcyclohexaneacetate*, $C_4H_9\cdot C_7H_{11}(OH)\cdot CH_2\cdot CO_2Et$, b. p. 129—131°/3 mm. This has been converted into *ethyl 1-methyl-4-tert.-butylcyclohexeneacetate*, b. p. 136—139°/10 mm.; the corresponding *acid* has b. p. 174—177°/10 mm., and the *chloride*, b. p. 127—128°/8 mm. *Ethyl* 1-methyl-4-tert.-*butylcyclohexaneacetate* has b. p. 146—149°/14 mm.; the corresponding *acid* has b. p. 173—176°/12 mm., and the *chloride*, b. p. 134—136°/13 mm.

These new chlorides give rise to the following ketones when treated with magnesium methyl iodide: 1-*Acetonyl*cyclo*hexene*,

$$C_6H_9\cdot CH_2\cdot COMe,$$

b. p. 79—80°/11 mm.; *semicarbazone*, m. p. 176°. *Acetonyl-2-methyl*cyclo*hexene*, b. p. 212°; *semicarbazone*, m. p. 170°. *Acetonyl-3-methyl*cyclo*hexene*, b. p. 206—207°; *semicarbazone*, m. p. 154°. 1-*Acetonyl*-*methyl*cyclo*hexene*, b. p. 208°; *semicarbazone*, m. p. 160—161°. *Acetonylmethylbutyl*cyclo*hexene*, b. p. 135—136°/10 mm.; *semicarbazone*, m. p. 206°.

W. O. W.

Action of the Chloroanhydride of *cyclo*Propanecarboxylic Acid on Benzene in Presence of Aluminium Chloride. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1163—1173).—The author has confirmed the formation of benzoyl*cyclo*propane by the decomposition of benzoyl*cyclo*propanecarboxylic acid (Perkin), and shows that this ketone is also obtained by the interaction of the chloroanhydride of *cyclo*propanecarboxylic acid and benzene in presence of aluminium chloride at 35—60°. Benzoyl*cyclo*propane, obtained by the latter method, gives a γ-benzoylpropyl bromide, m. p. 35°, whilst this compound when prepared from the benzoyl*cyclo*propane given by Perkin's method has m. p. 30·5°; this difference is not explained. The action of potassium hydroxide on γ-benzoylpropyl bromide yields benzoyl*cyclo*propane.

m-*Nitrobenzoyl*cyclo*propane*, $NO_2\cdot C_6H_4\cdot CO\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, separates from methyl alcohol in rectangular plates, m. p. 77°, and on reduction with tin and hydrochloric acid yields a crystalline *base*, m. p. 97—98°, the diazo-compound of which combines with naphthols, forming scarlet azo-colouring matters.

cyclo*Propylbenzylamine*, $NH_2\cdot CHPh\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, obtained by reducing the oxime of benzoyl*cyclo*propane in alcoholic solution with sodium, has b. p. 234·7—235°/749 mm., D_0^0 0·9996—1·0019, $D_0^{?}$ 0·9884, D_0^{20} 0·9843, n_D 1·5353—1·5360. The *hydrochloride*, m. p. 220—221°, *platinichloride*, $(C_{10}H_{11}NH_2)_2,H_2PtCl_6$, m. p. 177° (decomp.), and the *thiocarbamide*, $NHPh\cdot CS\cdot NH\cdot C_{10}H_{11}$, m. p. 124°, were prepared. Oxidation of the amine by means of permanganate yields benzoyl*cyclo*propane.

*Phenyl*cyclo*propylmethylcarbinol*, $OH\cdot CPhMe\cdot CH<\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, obtained by the interaction of benzoyl*cyclo*propane and magnesium methyl

iodide, has b. p. 241—242°/761 mm., 151—152°/51 mm., $D_4^{[illegible]}$ 1[illegible], n_D 1·5350.

a-Phenyl-a-cyclopropylethylene, $CH_2{:}CPh{\cdot}CH{<}\begin{matrix}CH_2\\|\\CH_2\end{matrix}$, prepared by the action of acetic acid on the preceding compound, has b. p. 211—213°/758 mm., D_0^{19} 0·9553, n_D 1·5497, and gives a golden-yellow coloration with a drop of concentrated sulphuric acid.

T. H. P.

Aromatic Amino-ketones. FRANZ KUNCKELL (*Ber. deut. pharm. Ges.*, 1911, 21, 419—456).—Various amino-ketones, in the form of their acetyl derivatives, have been prepared by heating acetanilide and an acyl halide with aluminium chloride in carbon disulphide and decomposing the resulting aluminium double compound with very dilute hydrochloric acid at 0°; the hydrolysis of the acetyl derivative is effected by 20% hydrochloric acid. It seems essential to success in the process that the acyl halide should have a b. p. exceeding 80—90°, or should be halogenated; for instance, the method fails with acetyl chloride or *iso*butyryl chloride, but yields good results with acetyl bromide or chloroacetyl chloride.

p-*Aminopropiophenone*, $NH_2{\cdot}C_6H_4{\cdot}COEt$, m. p. 140°, yellow needles, forms an *acetyl* derivative, m. p. 161°, *hydrochloride*, m. p. [illegible], *sulphate*, m. p. 225°, *oxime*, m. p. 153°, and *ethyl carbamate*, m. p. 15[illegible]. It reacts with carbonyl chloride in benzene to form *di*-p-*propionylphenylcarbamide*, $CO(NH{\cdot}C_6H_4{\cdot}COEt)_2$, m. p. 271°, whilst its hydrochloride reacts with hot aqueous potassium cyanate to form p-*propionylphenylcarbamide*, m. p. 218°.

p-*Aminobutyrophenone*, m. p. 84°, colourless needles, forms an acetyl derivative, m. p. 142°, *hydrochloride*, m. p. 178°, *sulphate*, m. p. 21[illegible], *ethyl carbamate*, m. p. 128°, and *benzoyl* derivative, m. p. 17[illegible]. p-*Butyrylphenylcarbamide* and *di*-p-*butyrylphenylcarbamide* have m. p. 194° and 235° respectively.

ω-*Chloro*-p-*acetylaminoacetophenone*, $NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Cl$, m. p. 212°, yields *p*-acetylaminobenzoic acid by oxidation, and forms the following derivatives in consequence of the reactivity of the chlorine atom: p-*Acetylaminophenyl phenoxymethyl ketone*,

$$NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OPh,$$

m. p. 145°; p-*acetylaminobenzoylmethyl acetate*,

$$NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}OAc,$$

m. p. 162° (the hydrolysis of which yields p-*acetylamino*-ω-*hydroxyacetophenone*, m. p. 176°, *phenylhydrazone*, m. p. 223°); p-*acetylaminobenzoylmethylbenzoate*, m. p. 200—201°; and p-*acetylamino*-ω-*phthaliminoacetophenone*, $NHAc{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2{\cdot}N{<}\begin{matrix}CO\\CO\end{matrix}{>}C_6H_4$, m. p. 27[illegible].

By treatment with nitric acid, D 1·5, at 0°, ω-chloro-*p*-acetylaminoacetophenone yields ω-*chloro*-m-*nitro*-p-*acetylaminoacetophenone*, yellow crystals, m. p. 120°; ω-*chloro*-m-*nitro*-p-*aminoacetophenone*, m. p. 1[illegible], obtained by its hydrolysis, yields *m*-nitro-*p*-aminobenzoic acid on oxidation. The bromination of ω-chloro-*p*-acetylaminoacetophenone in chloroform at 100° yields ω-*chloro*-2 : 5-*dibromo*-4-*acetylaminoacetophenone*, m. p. 137°, the oxidation of which by alkaline hydrogen peroxide yields 2 : 5-*dibromo*-4-*aminobenzoic acid*, m. p. above 350°;

...ic acid yields 2 : 5-dibromobenzoic acid and *p*-dibromobenzene by the successive elimination of the amino- and the carboxyl groups. ω-*Chloro-p-aminoacetophenone*, m. p. 146°, obtained by the hydrolysis of its acetyl derivative, forms a *hydrochloride* and *benzoyl* derivative, m. p. 177°. It reacts with potassium acetate and potassium benzoate respectively to form p-*aminobenzoylmethyl acetate*,

$$NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_3,$$

m. p. 135°, and the corresponding *benzoate*, m. p. 188°; the hydrolysis of the former yields p-*amino*-ω-*hydroxyacetophenone*,

$$NH_2\cdot C_6H_4\cdot CO\cdot CH_2\cdot OH,$$

m. p. 165° (*phenylhydrazone*, m. p. 199°).

By bromination in glacial acetic acid at 70°, ω-chloro-*p*-acetylaminoacetophenone yields ω-*chloro*-ω-*bromo*-p-*acetylaminoacetophenone*,

$$NHAc\cdot C_6H_4\cdot CO\cdot CHClBr,$$

m. p. 162°, which is converted into *p*-acetylaminobenzoic acid by oxidation and into ω-*chloro*-ω-*bromo*-p-*aminoacetophenone*, m. p. 80·5° (*hydrochloride*, m. p. 182°), by hydrolysis. By diazotisation and treatment with cuprous cyanide, ω-chloro-*p*-aminoacetophenone yields p-*chloroacetylbenzonitrile*, $CN\cdot C_6H_4\cdot CO\cdot CH_2Cl$, m. p. 98—100°, which is converted into the corresponding *acid*, m. p. 210°, by hydrolysis.

Chloroacetyl chloride, *m*-chloroacetanilide, and aluminium chloride react in carbon disulphide to form ω-m-*dichloro*-p-*acetylaminoacetophenone*, $NHAc\cdot C_6H_3Cl\cdot CO\cdot CH_2Cl$, m. p. 146—147°, which has been converted successively into 2-chloro-4-aminobenzoic acid and 2-chloro-4-hydroxybenzoic acid, and yields by hydrolysis ω-m-*dichloro*-p-*aminoacetophenone*, m. p. 96—97° (*hydrochloride*, m. p. 178°). In a similar manner, chloroacetyl chloride and *m*-bromoacetanilide yield ω-*chloro*-m-*bromo*-p-*acetylaminoacetophenone*, m. p. 113°, which is converted into the *amino*-compound, m. p. 97—98° (*hydrochloride*, m. p. 180°), by hydrolysis and into 2-bromo-4-aminobenzoic acid by oxidation. Chloroacetyl chloride and *o*-acetotoluidide yield ω-*chloro*-3-*acetylamino*-4-*methylacetophenone*, $NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2Cl$, m. p. 160°, which is converted by oxidation, hydrolysis, and diazotisation successively into o-*acetylamino*-p-*toluic acid*, m. p. 267—270° (decomp.), *o*-amino-*p*-toluic acid, and *p*-toluic acid; it yields ω-*chloro*-ω-*bromo*-3-*acetylamino*-4-*methylacetophenone*, m. p. 110°, by bromination in acetic acid, and reacts with potassium acetate or benzoate to form an *acetate*,

$$NHAc\cdot C_6H_3Me\cdot CO\cdot CH_2\cdot O\cdot CO\cdot CH_3,$$

m. p. 90°, or *benzoate*, m. p. 130°. The nitration of ω-chloro-3-acetylamino-4-methylacetophenone yields a *nitro*-compound, m. p. 204°, the constitution of which is proved by its conversion ultimately into *o*-nitro-*p*-toluic acid.

ω-*Chloro*-5-*acetylamino*-3-*methylacetophenone*, m. p. 145°, yields m-*chloroacetyl*-m-*toluidine*, m. p. 132°, by hydrolysis. C. S.

α-Aminoisobutyrophenone, $NH_2\cdot CMe_2\cdot COPh$. SIEGMUND GABRIEL (*Ber.*, 1911, **44**, 3091—3092).—When kept for three weeks, α-aminoisobutyrophenone (this vol., i, 212) is converted into a crystalline *substance*, $C_{20}H_{27}O_2N_3$, which separates from light petroleum in lustrous, glassy, flat, obliquely-cut needles or rhombohedral crystals,

m. p. 105—106°. An aqueous solution of the compound becomes strongly alkaline when boiled with water, owing to reconversion into the original amino-ketone. It dissolves in warm hydrochloric acid, yielding *a*-amino*iso*butyrophenone hydrochloride, which forms a *platinichloride*, $(C_{10}H_{13}ON)_2H_2PtCl_6$, m. p. 205—206°, with previous sintering at 195°. F. B.

Oxidation of Aniline. III. RIKŌ MAJIMA and YOSHIHIKO AOKI (*Ber.*, 1911, 44, 3080—3084. Compare this vol., i, 216).—By the oxidation of aniline with lead peroxide, Börnstein (Abstr., 1901, i, 375) obtained a compound, which he considered to be 2-amino-*p*-benzoquinonedianil. The compound is readily prepared by oxidising aniline in aqueous acetic acid solution at 0° with lead peroxide. Determinations of the molecular weight and analysis of its hydrochlorides show that it has the composition $C_{24}H_{20}N_4$, and not $C_{18}H_{15}N_3$. From its solubility in organic solvents, and the fact that it yields azophenine when heated with aniline in glacial acetic acid solution, the authors conclude that it has the constitution:

$$NPh:C<\begin{matrix}CH:C(NHPh)\\C(NH_2)=CH\end{matrix}>C:NPh.$$

2-Amino-5-anilino-*p*-benzoquinonedianil forms a *monohydrochloride*, $C_{24}H_{20}N_4,HCl$, and a *dihydrochloride*, $C_{24}H_{20}N_4,2HCl,3H_2O$; the *acetyl* derivative, $C_{26}H_{22}ON_4$, crystallises in long, bluish-red prisms, m. p. 212°. F. B.

Binary Systems of which One Component is an Organic Compound and the Other an Inorganic Salt. BORIS N. MENSCHUTKIN (*J. Chim. Phys.*, 1911, 9, 538—558. Compare this vol., i, 65).—A résumé of the author's work since 1903 on the additive organic compounds of magnesium, aluminium, and calcium haloids. R. J. C.

Photochemical Reactions of the Nitrophenylindones. I. MARUSSIA BAKUNIN and E. LANIS (*Gazzetta*, 1911, 41, ii, 155—184).—4-Nitro-2-phenylindone, when kept in sunlight, yields a substance, m. p. 320—325° (decomp.), which has the same percentage composition and is very indifferent to chemical reagents. Solutions of 4-nitro-2-phenylindone in various solvents, when exposed to light, deposited crystalline substances (apparently mixtures) of different and inconstant melting points. From the ethereal solution three substances are produced, which cannot be separated by recrystallisation, but on melting the mixture of all three the substance of m. p. 218° is converted into 4-nitro-2-phenylindone, which can be removed. From the remainder, two substances can be obtained, one having m. p. 280°, and the other m. p. about 320°; the latter is identical with the substance obtained from 4-nitro-2-phenylindone without a solvent. The products obtained in the case of other solvents were similar to the three just described.

6-Nitro-2-phenylindone remains unchanged in sunlight, but when its

solutions are exposed to light, mixtures of crystalline substances are produced. In the case of the benzene solution the product was separated into three substances, m. p. 227—229°, about 280°, and above 300° respectively.

In the formation of 4-nitro-2-phenylindone from 4-nitro-α-phenylcinnamic acid and phosphoric oxide in chloroform, a small quantity of a yellow, crystalline substance, m. p. 286°, is obtained.

R. V. S

Chloroiminoquinones. LEMUEL CHARLES RAIFORD (*Amer. Chem. J.*, 1911, **46**, 417—456).—Stieglitz and Earle (Abstr., 1904, i, 39) have described stereoisomeric chloroimino-acid ethers, and Stieglitz and Peterson (Abstr., 1910, i, 323; this vol., i, 879) have prepared stereoisomeric chloroimino-ketones. In the present paper, an account is given of experiments undertaken with the object of determining whether stereoisomerism could be observed in the chloroiminoquinones. Six chloroiminoquinones of a structure which should admit of the formation of stereoisomerides have been studied, but in no case was stereoisomerism discovered.

2-*Bromo-4-aminophenol*, m. p. 165°, crystallises in pale brown needles; its *hydrochloride* darkens at 225°, but does not melt.

2-*Bromo-4-chloroiminoquinone*, $O\!:\!C_6H_3Br\!:\!NCl$, prepared by the action of hypochlorous acid on 2-bromo-4-aminophenol, forms yellow crystals, and decomposes at about 60°.

2-*Chloro-6-bromo-4-aminophenol*, m. p. 181°, obtained by reducing the corresponding nitrophenol with stannous chloride, crystallises in thin plates, and is probably identical with the compound obtained by Clark (Abstr., 1893, i, 321). 2-*Chloro-6-bromo-4-chloroiminoquinone*, m. p. 87—88°, forms yellow crystals.

2 : 4 : 6-*Trichloro*-m-*cresol*, m. p. 47°, prepared by the action of sodium hypochlorite on *m*-cresol, crystallises in colourless plates, and on oxidation is converted into 2 : 6-dichlorotoluquinone; the *acetate*, b. p. 273—274°, was obtained as a colourless, viscous liquid.

When a solution of 2 : 4 : 6-tribromo-*m*-cresol in glacial acetic acid is treated with sodium nitrite, 2 : 4-dibromo-6-nitro-*m*-cresol, m. p. 134° (decomp.), and 2 : 6-dibromo-4-nitro-*m*-cresol, m. p. 87°, are obtained in yields of 35% and 40% respectively. 2 : 4-Dibromo-6-amino-*m*-cresol has m. p. 176°; the corresponding *benzoylamino*-compound, m. p. 198°, forms colourless crystals. 2 : 4-*Dibromo-3-hydroxy-o-tolyl-6-urethane*, $OH\cdot C_6HMeBr_2\cdot NH\cdot CO_2Et$, m. p. 155°, obtained by the action of ethyl chlorocarbonate on 2 : 4-dibromo-6-amino-*m*-cresol in presence of sodium hydroxide, is a brown solid. 2 : 6-*Dibromo-4-chloroiminotoluquinone*, $O\!:\!C_6HMeBr_2\!:\!NCl$, m. p. 86°, forms yellow, hexagonal plates. 2 : 6-*Dibromo-4-amino*-m-*cresol*, m. p. 116—117°, crystallises in brown scales; its *hydrochloride* is described. 2 : 6-*Dibromo-4-benzoylamino*-m-*tolyl benzoate*, m. p. 188°, forms colourless crystals. 2 : 6-*Dibromo-3-hydroxy*-p-*tolyl-4-urethane* has m. p. 169°. 2 : 6-*Dibromo-4-acetylamino*-m-*tolyl acetate*, m. p. 216°, crystallises in long, silky needles. When 2 : 6-*dibromo-4-nitro*-m-*tolyl ethyl carbonate*, $NO_2\cdot C_6HMeBr_2\cdot O\cdot CO_2Et$, m. p. 43—45°, obtained by the action of ethyl chlorocarbonate on 2 : 6-dibromo-4-nitro-*m*-cresol in presence of

sodium hydroxide, is reduced with tin and hydrochloric acid, it is **converted into 2 : 6-dibromo-3-hydroxy-*m*-tolylurethane.**

Kehrmann and Tichvinsky (Abstr., 1899, i, 129) have shown that **4-chlorotoluquinoneoxime exists in two modifications,** which, on **reduction, give a chloroaminocresol, m. p. 204—205°,** identical **with that obtained by the reduction of the substance** produced by **chlorinating 6-nitro-*m*-cresol in glacial acetic acid solution.** Attempts **have been made to prepare stereoisomeric chloroiminoquinones** corresponding **with these oximes. A chloroaminocresol prepared** from 6-nitro-*m*-cresol **had m. p. 166—167°, and on oxidation gave a** chloroiminoquinone, **m. p. 87°, whilst that similarly obtained from** Kehrmann's **chloroaminocresol had m. p. 91°. It is shown that** these **compounds are 2-*chloro*- and 4-*chloro*-6-*chloroiminotoluquinone*** respectively.

4-*Chloro*-6-*benzoylamino*-m-*tolyl benzoate*, m. p. 220°, prepared from Kehrmann's chloroaminocresol, forms nearly colourless crystals. 4-*Chloro*-6-*chloroiminotoluquinone*, $O:C_6H_2MeCl:NCl$, m. p. 91°, obtained by the action of hypochlorous acid on Kehrmann's chloroaminocresol, crystallises in radiating needles.

4-*Chloro*-3-*chloroiminotoluquinone*, m. p. 65°, prepared in a similar manner from the chloroaminocresol obtained by the electrolytic reduction of 3-nitro-4-chlorotoluene, forms brown nodules.

When 2-*chloro*-6-*nitro*-m-*cresol*, $OH\cdot C_6H_2ClMe\cdot NO_2$, m. p. 133°, obtained by the chlorination of 6-nitro-*m*-cresol, is reduced with stannous chloride, it is converted into 2-*chloro*-6-*amino*-m-*cresol*, m. p. 166—167°, which forms colourless crystals; its *hydrochloride* darkens above 225°. The *acetate* of the corresponding *acetylamino*-compound has m. p. 178°. On oxidation, 2-chloro-6-amino-*m*-cresol yields o-*chlorotoluquinone*, m. p. 55°, which is readily reduced to o-*chlorotoluquinol*, m. p. 173°, crystallising in colourless leaflets. By the action of hypochlorous acid on 2-chloro-6-amino-*m*-cresol, 2-chloro-6-chloroiminotoluquinone, m. p. 87°, is obtained.

By the chlorination of *o*-nitrotoluene, a mixture of 2-chloro- and 4-chloro-6-nitrotoluene is produced. These compounds on electrolytic reduction are converted into 2-chloro- and 4-chloro-6-amino-*m*-cresol, which, on oxidation, yield *p*-chlorotoluquinone, m. p. 105°, and *o*-chlorotoluquinone, m. p. 55°.

E. G.

[Preparation of Condensation Products from *p*-Benzoquinone or α-Naphthaquinone.] RUDOLF LESSER (D.R.-P. 236074). —When the condensation products of quinones (or other diketo-derivatives) are reduced in alkaline solution with sodium hyposulphite, valuable dyes are produced. The *products* from dianilino-*p*-benzoquinone, $C_6H_2O_2(NHPh)_2$, chlorodianilino-*p*-benzoquinone, and chloranilanilide (from aniline and chloranil) are mentioned. The *compound*, $C_6Cl_2O_2(NH\cdot C_6H_4\cdot OMe)_2$, obtained from chloranil and *p*-anisidine, forms red needles with metallic lustre, and the *product*,

$$C_{10}H_5O_2\cdot NH\cdot C_6H_4\cdot OEt,$$

from *p*-phenetidine and α-naphthaquinone, glistening, metallic, reddish-brown needles.

F. M. G. M.

The Partial or Total Replacement of Halogens by Hydrogen in Polyhalogenated Aminoanthraquinones. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 236604).—When polyhalogenated aminoanthraquinones or their derivatives are treated with reducing agents (such as iron and acetic acid) in the presence of pyridine, one or more of the halogen atoms are displaced by hydrogen.

Under these conditions, 2:4-dibromo-1-aminoanthraquinone yields 2-bromo-1-aminoanthraquinone; 2:4-dibromo-1-methylaminoanthraquinone furnishes 2-bromo-1-methylaminoanthraquinone, and 1:3-dibromo-2-aminoanthraquinone gives 3-*bromo*-2-*aminoanthraquinone* in brownish-yellow, glistening leaflets. F. M. G. M.

Preparation of *p*-Dialkylaminobenzyl-1-aminoanthraquinone. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 236769).—When a mixture of 1-aminoanthraquinone and a tertiary aromatic amine is treated with formaldehyde, it yields a *p*-dialkylaminobenzyl-1-aminoanthraquinone of the general formula

$$C_6H_4<\substack{CO\\CO}>C_6H_3\cdot NH\cdot CH_2\cdot C_6H_4\cdot NR_2.$$

p-*Dimethylaminobenzyl*-1-*aminoanthraquinone*, $C_{23}H_{20}O_2N_2$, obtained when dimethylaniline is employed, has m. p. 211°, and forms orange-red crystals, whilst p-*diethylaminobenzyl*-1-*aminoanthraquinone*, m. p. 196°, crystallises from xylene in red prisms. F. M. G. M.

Preparation of Mixed Arylanthraquinonylcarbamides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 236979 and 236981).—Arylanthraquinonylcarbamides have previously been prepared; it is now found that the reaction takes place when arylcarbamyl chlorides react with aminoanthraquinones. The *product* obtained by boiling a nitrobenzene solution of 2-aminoanthraquinone with diphenylcarbamyl chloride in the presence of sodium acetate forms yellow crystals, which does not fuse below 300°; this reaction is capable of wide extension. The second patent states that when β-aminoanthraquinone is heated with phenylurethane, a yellow powder separates from the cooled mixture, which has the properties of *phenyl-β-anthraquinonylcarbamide*. F. M. G. M.

Conversion of 1:2-Benzanthraquinone (Naphthanthraquinone) into Anthraquinone-1:2-dicarboxylic Acid. ROLAND SCHOLL and EMIL SCHWINGER (*Ber.*, 1911, 44, 2992—2998).—*Anthraquinone*-1:2-*dicarboxylic acid*, $C_6H_4<\substack{CO\\CO}>C_6H_2(CO_2H)_2$, required for the synthesis of 1:2-phthaloylanthraquinone, has been obtained by the oxidation of 1:2-benzanthraquinone. By oxidation by potassium permanganate in neutral solution, diphthalylic acid and anthraquinone-1:2-dicarboxylic acid are both formed, but only in small amount (compare Graebe and Peter, Abstr., 1905, i, 704). However, when a 5% solution of 1:2-benzanthraquinone in concentrated sulphuric acid is added to twice the weight of hot water and the nearly boiling mixture is oxidised by solid potassium permanganate, anthraquinone-

1 : 2-dicarboxylic acid is formed in 75·5% yield. The same acid is obtained in about 22% yield when the oxidation is effected by nitric acid, D 1·15, at 190—195°.

Anthraquinone-1 : 2-dicarboxylic acid crystallises in pale yellow needles containing H_2O, yields anthraquinone by distillation with calcium oxide and a little water, and changes at its m. p., 267—268°, into the *anhydride*, $C_{16}H_6O_5$, m. p. 319—321°, yellow prisms and leaflets, which is converted by ammonia at 225—235° into the *imide*, m. p. 293°, yellow needles. C. S.

Relation between Bisnitroso-compounds and Arylnitroso-hydroxylamines. EUGEN BAMBERGER (*Ber.*, 1911, **44**, 3066—3072). —According to Piloty (Abstr., 1902, i, 734) the colourless, bimolecular *C*-nitroso-compounds and the coloured, unimolecular nitroso-compounds are to be considered as belonging to the same class.

This view is supported by the author, who finds that chloroform, benzene, and glacial acetic acid solutions of certain typical bimolecular nitroso-compounds (bisnitrosylbenzyl, *d*-bisnitrosocarone, *iso*safrol-ψ-nitrosite, and anethole-ψ-nitrosite) acquire a blue or bluish-green colour when heated, and accordingly must contain the nitroso-compound in the unimolecular form.

An explanation is also given of the transformation of bisnitroso-carone, by the action of hydrochloric acid, into chlorocarone and caronebisnitrosylic acid (caronenitrosohydroxylamine) observed by Baeyer (Abstr., 1895, i, 379).

The first stage in the action consists in the dissociation of bisnitroso-carone into the unimolecular form, which under the influence of hydrogen chloride is converted into chlorocarone and nitroxyl: $C_{10}H_{15}O{\cdot}NO + HCl = C_{10}H_{15}OCl + NOH$. The latter compound then unites with a second molecule of the nitroso-compound to form caronebisnitrosylic acid, $C_{10}H_{15}O{\cdot}N(OH){\cdot}NO$.

The evanescent blue coloration observed on acidifying an alkaline solution of nitroethane is considered by the author to be due to the formation of either nitrosoethyl alcohol, NO·CHMe·OH, or the ψ-nitrile, $NO_2{\cdot}CHMe{\cdot}NO$. F. B.

Transformations of Thujane. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1157—1163).—In the preparation of thujane by the oxidation of thujylhydrazine (this vol., i, 71), the purification of the latter by means of its hydrochloride may lead to the partial inversion of the thujylhydrazine, and hence of the thujane, if any excess of acid is present with the hydrochloride; thus, it was found that the thujane from the pure thujylhydrazine had $[\alpha]_D$ +53·41°, whilst two preparations from the crude hydrazine had $[\alpha]_D$ +69·29° and +73·07° respectively.

When boiled with dilute sulphuric acid (1 : 6), thujane remains unchanged, whilst in a sealed tube the rotation is slightly lowered.

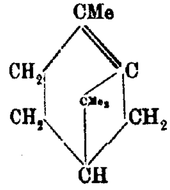
The action of hydrobromic acid on thujane for a short time yields an unstable bromo-derivative, but prolonged action gives a more stable, inactive *bromo*-compound, $C_{10}H_{19}Br$, b. p. 111—112°/19 mm., D_0^{20} 1·1812, n_D 1·4897, which is not decomposed when boiled with aqueous-alcoholic

potassium hydroxide. Reduction of this compound in 80% alcohol by means of a copper-zinc couple yields a *hydrocarbon*, $C_{10}H_{20}$, b. p. 157°/746 mm., D_4^{20} 0·7923, n_D 1·4377. The formation of this hydrocarbon, which is isomeric with menthane, indicates that the action of hydrobromic acid on thujane leads to the rupture of the trimethylene ring with formation of a *cyclo*pentane derivative, probably of the structure: $CHMe_2{\cdot}CBr{<}{\begin{array}{l}CH_2{-}CH_2\\ CHMe{\cdot}CHMe\end{array}}$. As the stable and the unstable bromo-derivatives give one and the same unsaturated hydrocarbon on decomposition, it is to be assumed that they are structurally identical, and that the difference in stability depends on stereoisomerism of the cis- and trans-type.

The bromo-compound stable to alcoholic potassium hydroxide is decomposed by distillation with quinoline, giving the unsaturated, inactive *hydrocarbon*, $C_{10}H_{18}$, b. p. 162—164°/755 mm., D_0^{20} 0·8108, n_D 1·4527. The similar *hydrocarbon*, $C_{10}H_{18}$, obtained by the action of potassium hydroxide on the unstable bromo-derivative, has b. p. 163—164°/755 mm., $D_4^{18·5}$ 0·8131, n_D 1·4540, $[\alpha]_D$ +2·88°, whilst the isomeric hydrocarbon prepared by the action of potassium hydroxide on the iodo-compound has b. p. 162·5—163·5°/751 mm., D_0^{20} 0·8111, n_D 1·4527, $[\alpha]_D$ +0·2°. Each of these three hydrocarbons gives a raspberry-red coloration with acetic acid. These hydrocarbons are probably of identical structure, which should be one of the three following: $CMe_2{:}C{<}{\begin{array}{l}CH_2{-}CH_2\\ CHMe{\cdot}CHMe\end{array}}$, $CHMe_2{\cdot}C{<}{\begin{array}{l}CH_2{-}CH_2\\ CMe{\cdot}CHMe\end{array}}$, and $CHMe_2{\cdot}C{<}{\begin{array}{l}CH{-}CH_2\\ CHMe{\cdot}CHMe\end{array}}$.

Another isomeric *hydrocarbon*, $C_{10}H_{18}$, obtained by converting thujane into the dibromo-compound, $C_{10}H_{18}Br_2$, and decomposing the latter with aqueous-alcoholic potassium hydroxide, has b. p. 162—164°/760 mm., D_0^{20} 0·8163, n_D 1·4520, $[\alpha]_D$ +23·62°. T. H. P.

Catalytic Isomerisation of α-Pinene. NICOLAI D. ZELINSKY (*Ber.*, 1911, **44**, 2782—2784. Compare Zelinsky and Glinka, this vol., i, 870).—α-Pinene (obtained by fractionation of French turpentine) yields an isomeride when treated with hydrogen in presence of palladium black from palladium chloride. This *iso*pinene has b. p. 158·5—159·5°, D_4^{20} 0·8573, n_{20} 1·4641, $[\alpha]_D$ −38·09°. It does not absorb hydrogen chloride, and a nitrosochloride could not be prepared from it. The author supposes the substance to be produced by dehydrogenisation of the hydropinene first formed, and assigns to it the annexed formula.



The same α-pinene, however, when treated with hydrogen for four weeks under the pressure of the head of acid in a Kipp's apparatus and in the presence of palladium black from palladium ammonium chloride, yields pinene of b. p. 167·5—168°/748 mm. Hydrogenisation of lævorotatory pinene by Sabatier's method gave

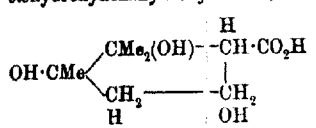
a hydropinene of b. p. 168—168·5° (corr.), D_4^{20} 0·8542, n_{20} 1·46[illegible], $[\alpha]_D$ −13·3°, and another *hydrocarbon*, $C_{10}H_{18}$, b. p. 163·5—16[illegible]/750 mm., D_4^{20} 0·8512, n_{20} 1·4580, $[\alpha]_D$ −9·58°. R. V. S.

isoLaurolene. IWAN L. KONDAKOFF and I. SCHINDELMEISER (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 992—1000).—Damsky (Abstr., 1888, 293) obtained *iso*laurolene by distilling the ammonium salt of sulphocamphylic acid in presence of ammonium chloride, but did not indicate the proportions of the two salts used. The authors have investigated this reaction, which they carried out in a current of carbon dioxide, and as molecular proportions of the two salts gave but little hydrocarbon, 2 mols. of ammonium chloride were taken per mol. of sulphocamphylate. The latter should be crystallised from [illegible] ammonia solution to prevent hydrolysis.

Sulphocamphylic acid, obtained by the action of sulphuric acid on camphoric anhydride, gave m. p. 162—164°, the value 160—165° having been given by earlier workers.

The products obtained by distilling the mixture of ammonium chloride and sulphocamphylate were: *iso*laurolene; di*iso*propenyl; a ketone giving an oxime, m. p. 116—118°, and a bromide, softening at 76°, m. p. 79°; β-hydroxyhexahydro-xylic acid (compare Lees and Perkin, Trans., 1907, 79, 332), and possibly other cyclic hydrocarbons.

The reactions probably proceed as follows: The sulphocamphylic acid combines with the hydrogen chloride yielded by dissociation of the ammonium chloride, giving two compounds, which lose hydrogen chloride, with formation of α- and β-campholytic acids. The former of these readily undergoes isomeric change into the latter, which loses carbon dioxide and gives *iso*laurolene. These two acids may also be transformed, by way of their hydrochlorides, into campholactones, including ψ-campholactone; this then gives (1) the lactone of *cis*hydroxyhexahydroxylic acid, and from it the corresponding acid, and (2) xylic acid. The hydroxy-acids corresponding with the campholactones, and, to some extent, the acid corresponding with ψ-campholactone, in consequence of hydration, dehydration,



and loss of carbon dioxide and other groups, give a pinacone (annexed scheme), this pinacone then undergoing dehydration to diisopropenyl. These hydroxy-acids also probably give an isomeride of camphorone or the latter itself.

The various products obtained are being investigated. T. H. P.

Santene and its Hydrohalides. IWAN L. KONDAKOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1107—1116).—The author has previously (Abstr., 1910, i, 327) drawn the conclusion that, on loss of hydrogen chloride, true bornyl chloride and also fenchyl chloride do not yield methylenecamphene and methylenefenchene immediately, but that they give, firstly, a mixture of bornylene and cyclene, and fenchobornylene and fenchocyclene respectively, these then undergoing isomeric change into (1) methylenecamphene, *iso*-

cyclene, and isocamphene, and (2) fenchene, fenchocyclene, and isofenchene. May (*Diss.*, Berlin, 1910) arrived at a similar conclusion. The present paper records certain observations made in the attempt to confirm the above statement experimentally.

Two natural santenes were employed: that from sandalwood oil (compare Müller, Abstr., 1900, i, 677), and that from the essential oil of the fir (compare Aschan, Abstr., 1908, i, 94), these two being regarded as identical and pure. It is found that, in the latter case, santene cannot be obtained pure by fractionation, since the lower fractions of the oil contain a hydrocarbon with a lower boiling point than santene, whilst the neighbouring fractions with higher boiling points contain camphene and pinene. The hydrocarbon of low b. p. distils at 105—110°, does not change in the air, and is not oxidised by permanganate solution; its nature is under investigation. A hydrocarbon, C_7H_{10} (?), with this b. p. was obtained by Müller (*loc. cit.*) by the dry distillation of calcium teresantalate, either alone or mixed with calcium acetate.

When treated with concentrated hydrochloric acid, the various fractions of fir-santene exhibit the following behaviour: (1) the fraction, b. p. 105—125°, is turned brown, and yields principally a black, caoutchouc-like mass, and hence very little chloro-derivative; (2) that with b. p. 125—142° is coloured yellow, owing to the admixture with that of lower b. p., and gives a chloro-compound liquid at the ordinary temperature, and (3) that boiling at 142—147° remains colourless, and yields a mixture of liquid and solid chloro-derivatives. The santene hydrochloride obtained is identical with norbornyl chloride, and consists of two isomerides, melting at 14° and 81° respectively, assuming the m. p. 81°, given by Müller and by Aschan, to be that of the pure isomeride. Using conditions for its preparation different from those of these authors, it is found that santene hydrochloride from santalol has a lower melting point than 81°. This hydrochloride, when pure, remains unchanged for a long time, but is converted into the isomeride with the lower melting point under the influence of hydrochloric acid.

Contrary to Semmler's statement, the hydrochloride with high melting point is very stable to concentrated alcoholic potassium hydroxide at the ordinary temperature. On the water-bath it undergoes only partial decomposition in five hours, whilst in a sealed tube at 170° it yields in the same space of time the two products: (1) an optically inactive *hydrocarbon*, C_9H_{14}, b. p. 138·5—142·5°, D^{18} 0·8714, n_D 1·46761, and (2) an ether, b. p. about 195°.

The action of concentrated hydrobromic acid on santalol-santene yields a solid hydrobromide, melting in some cases at 25° and in others at 18°, and gradually undergoing change into an inactive liquid *isomeride*, $C_9H_{15}Br$, b. p. 79—81°/8 mm., D^{18} 1·273, n_D 1·50573, which either corresponds with the hydrochloride of lower melting point or represents a mixture of the two isomerides.

When treated with concentrated alcoholic potassium hydroxide, both the liquid and solid hydrobromides yield a mixture of santene and the ether, b. p. 195°. The formation of this ether, in this and also in the preceding case, is regarded as due to condensation.

Oxidation of the santene from the hydrohalides by means of permanganate gives a hydrocarbon, b. p. 137·5—142·5°, santene glycol, and a small quantity of a fragrant-smelling substance. Oxidation of santene from santalol gives the glycol in larger proportion and more rapidly.

The acetyl derivative, C_9H_{15}·OAc, of the santenol synthesised from sandalol santene at the ordinary temperature has b. p. 85—89°/8 mm., D^{20} 0·9859, n_D 1·45929, and is optically inactive. T. H. P.

Action of Nitrosyl Chloride on the Essential Oil of Bupleurum fructicosum. Nitrosochlorides. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 190—196). —The previous attempts to prepare a nitrosochloride from the essential oil of *Bupleurum fructicosum* (Francesconi and Sanna, this vol., i, 896) by the method used by Wallach (Abstr., 1889, 1069) for carvene having been unsuccessful, the oil was separated into seventeen fractions by distillation in a vacuum, but the method yielded no better results when employed on the separate fractions. By modifying the procedure, however, by omitting the water and acetic acid, a nitrosochloride has been prepared from all the fractions. A well-cooled mixture of an alcoholic solution of the oil with amyl nitrite or ethyl nitrite is well stirred and treated with a saturated alcoholic solution of hydrogen chloride in drops. The crude *nitrosochloride*, $C_{10}H_{16}ONCl$, obtained is an unstable substance, and, although its m. p. and rotatory power are fairly constant, it is a mixture of at least two nitrosochlorides, termed α and β, which have very different solubilities in chloroform. The more soluble α-nitrosochloride has m. p. 101—102°, $[\alpha]_D$ − 175°; the β-nitrosochloride has m. p. 100—101°, $[\alpha]_D$ − 285°. R. V. S.

Essential Oil of Bupleurum fructicosum, Linn. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 230—233. Compare this vol., ii, 1025; Francesconi and Sanna, this vol., i, 658, 896).—In the present paper an account is given of the fractional distillation of 10 litres of the essential oil. Seventeen fractions were collected, and the results are given of their examination in respect to refractive index, rotatory power, density, percentage composition, acidity, saponification number, etc. R. V. S.

$\Delta^{1,5}$-Dihydrocuminaldehyde [and] β-Phellandrene in the Essential Oil of Bupleurum fructicosum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 325—331. Compare preceding abstract).—It is shown that the dihydrocuminaldehyde previously obtained from the nitrosochloride from this essential oil is $\Delta^{1,5}$-dihydrocuminaldehyde. The terpene of the oil is β-phellandrene, although it has a greater rotatory power than this substance as obtained from other sources. It gives a nitrosochloride, which (like its nitrosite) has a rotatory power of opposite sign to its own, and decomposes with production of $\Delta^{1,5}$-dihydrocuminaldehyde. R. V. S.

Champaca Oil. BENJAMIN T. BROOKS (*J. Amer. Chem. Soc.*, 1911, **33**, 1763—1772).—The flowers of *Michelia champaca* yield 0·37% of an

essential oil, two specimens of which gave the following constants: D^{30} 0·9040 and 0·9107; n_D^{30} 1·4640 and 1·4688; ester number, 124 and 146; the ester number of the latter sample after acetylation was 199. The oil contains phenylethyl alcohol, cineole, *iso*eugenol, benzyl alcohol, benzoic and acetic acids, and a crystalline ketone, $C_{16}H_{20}O_5$, first described by Bacon (this vol., i, 73). This ketone has $[\alpha]_D^{30}$ $-82·5°$; the phenylhydrazone has m. p. 161°. By a study of the action of alcoholic potassium hydroxide on the ketone, it is shown that it is probably a succinic ester of ethyl alcohol and a ketonic alcohol, $C_{10}H_{12}O_2$, containing the group –CH:CH·CO–, and may therefore be represented by the formula $CO_2Et·CH_2·CH_2·CO_2·C_{10}H_{11}O$.

The essential oil of *Michelia longifolia* differs considerably from that of *M. champaca*, and gives the following constants: D^{30}_{30} 0·897, n_D 1·4470, and ester number 180; its most characteristic constituent is methyl or ethyl *a*-methylbutyrate.

The flowers of both species of *Michelia* contain an oxydase, and it is suggested that to such enzymes the formation of aldehydes and ketones in essential oils is largely due. E. G.

Essential Oil of Santolina chamæcyparissus, L. I. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 255—260).—The quantity of essential oil contained in the stem of the plant is small, but it is found in considerable quantity in the leaves. The extraction was effected by distillation in steam, and the yield varied from 0·2% to 1·15% of the material taken, the maximum being obtained just before flowering. The densities and the rotatory powers of the various products were not markedly different. The oil begins to distil at 176° at the ordinary pressure. At 15—20 mm., distillation was carried out from 94° to 111°, six fractions being collected. The earlier fractions contained a terpene, whilst in the later ones there are probably hydroaromatic oxygenated compounds. The saponification numbers showed the presence of an ester, and indications of the presence of ketones were obtained. The oil does not contain acids, alcohols, or phenols. R. V. S.

Essential Oil of Santolina chamæcyparissus, L. II. Action of Hydroxylamine. LUIGI FRANCESCONI and P. SCARAFÌA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 318—324. Compare preceding abstract). —By the action of hydroxylamine hydrochloride on the essential oil in aqueous-alcoholic solution in the presence of sodium hydrogen carbonate, the following substances are produced: (1) the hydroxylamine-oxime of a ketone, $C_{10}H_{16}O$; (2) an oxime of the same ketone; (3) an oxime of another ketone; (4) a hydroxylamine; (5) terpenes and other unaltered substances.

The terpene, after fractionation, has b. p. 165—170°, and appears to contain one double linking.

When the product of the reaction is distilled with steam, the distillate contains the two oximes and the hydroxylamine. The oximes can be removed by acidifying and redistilling. The *hydroxylamine* crystallises in hexagonal laminæ, m. p. 62—64°. When oxidised with mercuric oxide it yields a *nitroso*-compound, which is a colourless, crystalline substance, m. p. 60—62°: fused or in solution it is blue.

The *oximes* are liquids which reduce Fehling's solution after they have been boiled with hydrochloric acid, and at the same time this hydrolysis leads to the production of one or more carbonyl compounds.

The *hydroxylamineoxime*, $OH\cdot NH\cdot C_{10}H_{17}\!:\!N\cdot OH$, obtained by crystallisation from the original reaction product, forms large prisms or thin laminae, which on heating soften at 180—185° and melt at 190°; the liquid evolves gas and resolidifies, melting again at 260°. If the heating is slow, the conversion into the substance of m. p. 260° occurs directly, no previous fusion being observed. The hydroxylamine-oxime does not reduce Fehling's solution, unless it has been boiled previously with hydrochloric acid. It does not react with aldehydes. By the action of nitrous acid, a *dioxime*, $C_{10}H_{16}(N\cdot OH)_2$, is obtained; it forms small, lustrous prisms, m. p. 268° (decomp.). The *dibenzoyl-dioxime* has m. p. 150—155°. When the hydroxylamineoxime is kept at 190—200° for an hour or more, the above dioxime is obtained, and in addition the *amino-oxime*, $NH_2\cdot C_{10}H_{17}\!:\!N\cdot OH$, which crystallises in colourless prisms, m. p. 150°.

R. V. S.

Components of Essential Oils. Composition of the Essential Oils of Xanthoxylum aubertia (Evodia aubertia), and Xanthoxylum alatum. FRIEDRICH W. SEMMLER and F. SCHOSSBERGER (*Ber.*, 1911, **44**, 2885—2890).—The oil of *Xanthoxylum aubertia* was divided into three fractions. Fraction 1, b. p. 70—80°/16 mm., comprised 2—3%, and has D^{20} 0·8248, n_D 1·4977, α_D +30°. It is probaby an aliphatic terpene. Fraction 2, b. p. 115—130°/16 mm., comprised 80—90%. On purification it had the following properties: b. p. 119—123°/9 mm., D^{20} 0 8781, n_D 1·499, $[\alpha]_D$ -58°. It consists in part of a sesquiterpene, *evodene*, of the same type as limene; eugenol methyl ether is also present, and constitutes 40—60% of the crude oil. The third fraction is a solid, m. p. 85° (about 10% of the oil); it is phloroacetophenone dimethyl ether, $C_{10}H_{12}O_4$.

Xanthoxylum alatum.—The first fraction, b. p. 50—60°/9 mm., comprised 80% of the crude oil, and is possibly l-*sabinene*, but is provisionally termed *xanthoxylene*; it has D^{20} 0·84, n_D 1·47457, α_D −26°, and forms a *hydrochloride*, b. p. 83—87°/10 mm., D^{20} 0·959, n_D 1·4824, α_D −11°. The *hydrocarbon*, $C_{10}H_{18}$, obtained from this on reduction showed b. p. 52—58°/9 mm., D^{20} 0·8275, n_D 1·4582, α_D −17°. The ozonide on decomposition yielded an acid, b. p. 174—180°/10 mm. The corresponding *sabinene ketone* has b. p. 102—106°/14 mm., D^{20} 0·9612, n_D 1·47064, α_D +14°.

The second fraction, which only amounted to 5—10% of the crude oil, yields two semicarbazones, m. p. 210—211° and 221°. The former corresponds with cuminaldehyde.

The third fraction consisted of phloroacetophenone dimethyl ether, $CH{<}{\begin{matrix}C(OH)\cdot C(COMe)\\ C(OMe)=\!=\!=CH\end{matrix}}{>}C\cdot OMe$; it forms a monobromo-derivative, m. p. 187°, an acetyl derivative, m. p. 107°, and a methyl derivative, m. p. 103° (Schimmel & Co., *Report*, 1909; Abstr., 1909, i, 313).

E. F. A.

Apparently Reversible Character of the Vulcanisation Reaction of Caoutchouc by Sulphur. PAUL BARY and L. WEYDERT (*Compt. rend.*, 1911, **153**, 676—678).—The free and combined sulphur in a sample of vulcanised caoutchouc was estimated, and the former removed by extraction with acetone, or else separated by removing the gum with xylene. After heating the product at 145° for eight hours, the caoutchouc was again analysed in the same way. The results show that ordinary vulcanised caoutchouc is an equilibrium mixture, and that combined sulphur is set free on diminishing the osmotic pressure of the free sulphur. The reaction of vulcanisation is represented as $C_{10}H_{16} + S_2 \rightleftharpoons C_{10}H_{16}S_2$, but the numerical data obtained are not in agreement with the ordinary law of mass action, whatever hypothesis may be adopted as to the degree of polymerisation of the hydrocarbon. The conclusion drawn is that the hydrocarbon molecules having polymerised by union at the double linkings, on vulcanisation sulphur first becomes attached only to the terminal double linkings of a chain; further vulcanisation, therefore, can only occur after depolymerisation. W. O. W.

Preparation of Substances Resembling Caoutchouc. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235686).—When compounds of the general type $:C:C\cdot C:C:$, where the free valencies are saturated partly with hydrogen and partly with alkyl groups, are heated either in the presence or absence of condensing agents, they polymerise into substances like caoutchouc.

Piperylene, $CHMe:CH\cdot CH:CH_2$, when heated at 150° during twenty-four hours or at 90—100° during eight days, yielded a colourless, elastic *substance*, isomeric with natural caoutchouc.

Plastic masses of similar nature were obtained by heating δ-methyl-$\Delta^{\beta\gamma}$-pentadiene, $CMe_2:CH\cdot CH:CH_2$, at 200° during twenty-four hours, also from tetramethylerythrene, $CMe_2:CH\cdot CH:CMe_2$, and from the substance $CH_2<\begin{matrix}CH_2-CH\\ CH_2\cdot CH_2\end{matrix}>C\cdot CMe:CH_2$. F. M. G. M.

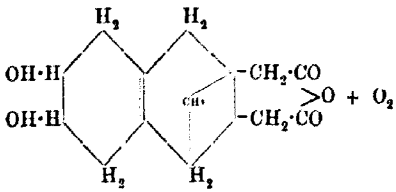
Clavicepsin, a New Glucoside from Secale cornutum. FRANCESCO MARINO-ZUCO and V. PASQUERO (*Gazzetta*, 1911, **41**, ii, 368—374).—When *Secale cornutum* is extracted with hot alcohol for several days, the alcoholic solution contains a syrup partly soluble in water. From the aqueous solution, the new glucoside, $C_{18}H_{34}O_{16},2H_2O$, can be isolated in the form of acicular crystals, m. p. 91°, or, when anhydrous, 198°. It has $[\alpha]_D^{20}$ +142·27°. It is not hydrolysed by emulsin, but with acids it yields 2 mols. of dextrose (identified as phenylhydrazone) and 1 mol. of mannitol (identified by isolation and analysis) according to the equation: $C_{18}H_{34}O_{16} + 2H_2O = 2C_6H_{12}O_6 + C_6H_{14}O_6$. R. V. S.

Picrotoxin. FRANCESCO ANGELICO (*Gazzetta*, 1911, **41**, ii, 337—349. Compare Abstr., 1910, i, 404, 577).—The action of hydriodic acid and phosphorus on either picrotin or picrotoxinin yields an acid, $C_{15}H_{18}O_4$, and a ketone, $C_{14}H_{16}O_3$, previously described. The reaction is accompanied by the evolution of carbon dioxide and a little carbon monoxide.

The action of alkaline permanganate on the acid $C_{15}H_{18}O_4$ gives (in addition to the acids $C_{15}H_{16}O_6$, $C_{13}H_{12}O_8$, and $C_{12}H_{12}O_7$) a small quantity of an *acid*, $C_{14}H_{16}O_6$, which forms small needles, m. p. 189°.

The acid $C_{13}H_{12}O_7$, m. p. 175°, is not a malonic derivative. When it is oxidised with chromic acid in the presence of 25% sulphuric acid it yields a dibasic *acid*, $C_{12}H_{12}O_7$, which crystallises in needles, m. p. 289—290° (decomp.), and gives a *silver* salt, $C_{12}H_{10}O_7Ag_2$.

The series of acids which has now been obtained from picrotin and from picrotoxinin is therefore: $C_{15}H_{18}O_4$, $C_{15}H_{16}O_6$, $C_{14}H_{16}O_6$, $C_{13}H_{12}O_8$, $C_{13}H_{12}O_7$, and $C_{12}H_{12}O_7$. The author suggests the annexed formula for picrotin. Picrotoxinin would then be the unsaturated (hexahydronaphthalene) derivative containing no hydroxyl groups, but having also the two oxygen atoms of unknown function.



With a view to determining the function of these oxygen atoms, experiments have been made on various products with phosphorus pentachloride. The monocarboxylic acid, $C_{15}H_{18}O_4$, remains unaltered. The halogenated ketone yields an oily, chlorinated product, which gives a phenylhydrazone, and the halogenated ketone also yields a small quantity of a *substance*, m. p. 168—169°. The ketone, $C_{14}H_{16}O_3$, gives the same results, but in this case the substance of m. p. 168—169° was analysed, and corresponds with the union of 2 mols. of ketone less $1H_2O$, or $C_{28}H_{26}O_3Cl_2$. The ketone, $C_{14}H_{16}O_3$, when distilled with zinc dust gives traces of a substance, probably a *hydrocarbon*, of which the *picrate* has m. p. 205—206°.

The nitro-acid, $C_{13}H_{15}O_5N$ (compare Abstr., 1910, i, 578), is accompanied by a small quantity of a *substance*, m. p. 86—87°. When reduced with ammonium sulphide in the warm, the nitro-acid gives the corresponding *amino*-acid, $C_{13}H_{17}O_3N,H_2O$, m. p. 175—176°. The amino-acid is oxidised by permanganate at the ordinary temperature, giving a *tribasic acid*, $C_7H_{10}O_6$, which crystallises in small needles, m. p. 95°, and gives a *silver* salt, $C_7H_7O_6Ag_3$. R. V. S.

Composition of Tannin. WILHELM STEINKOPF and JOHANN SARGARIAN (*Ber.*, 1911, 44, 2904—2906).—Iljin (Abstr., 1909, i, 505) has stated that tannin derived from the commercial product by repeated purification has the composition 54·13% C and 3·22% H, values which are not in agreement with those usually obtained or with Nierenstein's formula. A careful repetition of Iljin's experiments indicates values 52·69% C and 3·77% H, in full agreement with those of previous observers. E. F. A.

Bile Pigments. II. Urobilinogen of Urine and the Nature of Ehrlich's Aldehyde Reaction. HANS FISCHER and FRIEDRICH MEYER-BETZ (*Zeitsch. physiol. Chem.*, 1911, 75, 232—261. Compare this vol., i, 803).—Urobilinogen has been prepared from pathological

arise in a crystalline form, and identified with hemibilirubin by the crystallographic characters. A number of unstable pyrrole derivatives, including all the crystalline blood pigments and the bile pigments at present known, are converted into urobilin on decomposition, both in experiments in test-tubes and in the organism. All these unstable pyrrole compounds contain a hydrogen atom attached to one of the carbon atoms in the chain, and they all give the Ehrlich reaction with *p*-dimethylaminobenzaldehyde.

The urobilinogen and urobilin tests are not decisive when they are given after unnatural substances have been administered to the animal; urobilinogen, moreover, may be present in urine in considerable quantity without giving the aldehyde reaction.

Ehrlich has shown that certain pathological urines give an intense red coloration with dimethylaminobenzaldehyde in acid solution. The dye in question is now shown to be a dipyrrylphenylmethane dye formed by a secondary reaction from the corresponding leuco-base.

Ethyl 2:5-dimethylpyrrole-3-carboxylate condenses with anisaldehyde to form a colourless, crystalline substance, $C_{26}H_{32}O_5N_2$, m. p. 199—200 (corr.).

The pyrrole derivative also condenses with *p*-dimethylaminobenzaldehyde in acid alcoholic solution to a colourless, crystalline leuco-base, $C_{27}H_{35}O_4N_3$, m. p. 239°. On oxidation with ferric chloride, the dye is obtained; it forms a hard, dark red, lustrous mass, with a green reflex. The colour is stable towards acids, but altered by sodium hydroxide, although restored again on making the solution acid. It has the properties of a triphenylmethane dye.

The corresponding dye from hemibilirubin and *p*-dimethylaminobenzaldehyde is reddish-violet and very sensitive to alkali; dilute sodium carbonate changes the violet colour into brownish-yellow.

E. F. A.

Bile Pigments. III. Hemibilirubin and its Oxidation Products. HANS FISCHER and PAUL MEYER (*Zeitsch. physiol. Chem.*, 1911, 75, 339—349. Compare Abstr., 1911, i, 803).—Hemibilirubin has been found to exist in two forms, an acidic and a non-acidic. The latter is the pure hemibilirubin. The former, which dissolves in solutions of hydrogen carbonates with the evolution of carbon dioxide, has not yet been obtained pure.

By the reduction of bilirubin in alkaline solution by means of sodium amalgam, three products have been obtained, namely: (I) hemibilirubin, (II) the acidic form of hemibilirubin, and (III) a substance which has not yet been identified. On oxidation all three substances yield the imide of hæmatic acid, together with methylethylmaleinimide. Hæmatic acid only was found among the products of the oxidation of bilirubin.

From determinations of molecular weight, the authors draw the conclusion that the formulæ previously ascribed to hemibilirubin are incorrect, and propose either $(C_{16}H_{22}O_3N_2)_2$ or $C_{33}H_{44}O_6N_4$.

H. W.

Melanin Pigments of Animal Origin. MAURICE PIETTRE (*Compt. rend.*, 1911, 153, 782—785).—The material employed in this investigation was prepared by macerating sarcomatous tumours from horses, removing the cellular débris after cooling in ice, and separating the melanin pigment by centrifugation. When submitted to alkali hydrolysis the melanin yielded alanine, together with other crystalline amino-acids, the amount of which was insufficient for identification. The residual pigment had the composition C 61·72, H 4·39, N 9·4, S 1·6, Fe_2O_3 0·178%. Acid hydrolysis resulted in the separation of tyrosine (0·11%), leucine (2·95%), amorphous amino-acids (9·32%), and a pigment containing iron and sulphur, and having C 55·69, H 3·49, N 9·72%. The original melanin, therefore, appears to contain a protein group in union with a pigment.

W. O. W.

Action of Sulphurous Acid and of Sulphites on Various Dyes. HUGO WEIL, KARL DÜRRSCHNABEL and PAUL LANDAUER (*Ber.*, 1911, 44, 3172—3179. Compare Dürrschnabel and Weil, Abstr., 1905, i, 947).—Methylene-blue is at first unchanged by sulphurous acid, but, after a time, a *substance* separates in small quantity in well-formed yellow crystals of both basic and acid character having the composition $C_{32}H_{36}O_8N_6S_5,5H_2O$ or $4\frac{1}{2}H_2O$, corresponding with the entry of three sulpho-groups into two methylene-blue residues. Characteristic derivatives could not be obtained; oxidation with dichromate gives a blue dye; with acetic anhydride a green, hygroscopic powder is obtained.

Sodium sulphite forms leucomethylene-blue, a lustrous, bronze-coloured, crystalline intermediate product being also formed, which probably represents methylene-blue sulphite.

With sodium hydrogen sulphite the first product is a dull blue precipitate, which, after remaining three or four days or on warming, is converted into the yellow, crystalline precipitate of leucomethylene-blue-sulphonic acid, $C_{16}H_{19}O_8N_3S_2,2H_2O$. If the original mother liquors are allowed to evaporate at a low temperature, very soluble, lustrous, silver platelets are obtained, which instantly become blue on exposure to the air; this is regarded as a sulphaminic acid.

Sulphurous acid and nitromethylene-blue interact to form a *nitro-leucomethylene-blue-sulphonic acid*, $C_{16}H_{18}O_5N_4S_2$; this has pronounced acid properties, and forms a green dye on oxidation. The mother liquors contain basic substances, which are oxidised to blue compounds. When the *nitro-leuco-acid* is reduced with zinc and hydrochloric acid, the *zinc* salt of an *aminoleuco-acid*, $ZnC_{32}H_{38}O_6N_8S_4$, is formed; this gives a blue oxidation product.

With Meldola's-blue, sulphurous acid yields a brown, crystalline compound, $C_{18}H_{16}O_4N_2S$.

Phenylindamine and sodium hydrogen sulphite form lustrous, colourless plates of a *substance*, $C_{12}H_{13}O_6N_3S_2$; tolylindamine and phenyltolylindamine behave similarly, the product in each case being a *leucodisulphonic acid*. Phenyltetramethylindamine reacts with sodium hydrogen sulphite or sulphurous acid to form lustrous, colourless crystals of a *monosulphonic acid*.

Safranines are not decolorised by sulphurous acid; coloured salts

separate after a time, which appear to be a mixture of sulphite and sulphate. E. F. A.

Action of a Mixture of Allyl Bromide and Furfuraldehyde on Magnesium: Synthesis of Furylallylcarbinol. A. SEMENTSOFF and P. KONJUKOFF-DOBRYNIA (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 990—992. Compare Javorsky, Abstr., 1908, i, 753).—*Furylallylcarbinol*, $\begin{matrix}CH\cdot CH \\ \parallel \\ CH-O\end{matrix}\!\!>\!C\cdot CH(OH)\cdot CH_2\cdot CH{:}CH_2$, prepared by the interaction of magnesium, allyl bromide, and furfuraldehyde, is a colourless liquid, b. p. 96—97°/21 mm., $D_4^{20.5}$ 1·0424, $n_D^{20.5}$ 1·49192, which rapidly turns yellow. T. H. P.

7-Methoxy-3 : 4-dihydro-1 : 4-benzopyrone. ALEXEI E. TSCHITSCHIBABIN and I. V. NIKITIN (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1185—1189).—7-Methoxy-3 : 4-dihydro-1 : 4-benzopyrone,

$$OMe\cdot C_6H_3<\begin{matrix}O-CH_2 \\ | \\ CO\cdot CH_2\end{matrix},$$

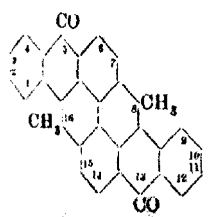
may be expected to lead to the formation of substances of the two structural formulæ which are at present regarded as the most probable for brazilin (compare Werner and Pfeiffer, *Chem. Zeitsch.*, 1904, **3**, 421; Perkin and Robinson, Trans., 1908, i, 489; von Kostanecki and Lampe, Abstr., 1902, i, 481).

The synthesis of this compound is effected in two stages: (1) the action of the sodium derivative of *m*-methoxyphenol on sodium β-iodopropionate gives sodium β-*m*-methoxyphenoxypropionate, which (2) is converted into 7-methoxydihydrobenzopyrone by the action of phosphoric oxide. The condensation of the pyrone with veratraldehyde, which should give a compound having a structure closely related to the Pfeiffer-Perkin formula for trimethylbrazilin, is being investigated.

β-m-*Methoxyphenoxypropionic acid*, $OMe\cdot C_6H_4\cdot O\cdot CH_2\cdot CH_2\cdot CO_2H$, separates from light petroleum in flat, shining needles, m. p. 82·5°; its *silver* salt was analysed.

3-*Methoxydihydrobenzopyrone*, $C_{10}H_{10}O_3$, crystallises from water in slender, colourless needles, m. p. 55°. T. H. P.

Synthetical Experiments in the Pyranthrone Series. ROLAND SCHOLL, JULIUS POTSCHIWAUSCHEG, and JOSEF LENKO (*Monatsh.*, 1911, **32**, 687—710).—Pyranthrone homologues have been prepared in which the alkyl groups are attached to the benzene nuclei between the two anthraquinone complexes. 2 : 2′-Diethyl-1 : 1′-dianthraquinonyl condenses in a similar manner to the dimethyl compound (Scholl, Abstr., 1910, i, 271), although at a higher temperature, forming 8 : 16-dimethylpyranthrone (annexed formula), isomeric with 6 : 14-dimethylpyranthrone (Scholl, *loc. cit.*; this vol., i, 656, 676). 2 : 2′-Di-*n*-propyl-1 : 1′-dianthraquinonyl behaves similarly, but the isomeric di-*iso*propyldianthraquinonyl did not undergo condensation. The last can only react to give an aldol-like condensation product, and



the fact that none such is formed precludes the formation of alkyl compounds as intermediate stages in the other condensations.

To prepare the 2-alkylanthraquinones, alkylbenzenes were condensed with phthalic anhydride in presence of aluminium chloride to 4-alkylbenzophenone-2′-carboxylic acids, these reduced to benzylbenzoic acids, condensed to alkylated anthrones, and oxidised to the corresponding anthraquinones.

In addition, *n*-propylbenzoylbenzoic acid was prepared by the Grignard reaction from *p*-iodo-*n*-propylbenzene, phthalic anhydride, and magnesium; it proved to be identical with the compound obtained by means of aluminium chloride, which in this instance does not cause isomerisation of the propyl group.

2-*n*-Propylanthraquinone could not be condensed to a homologue of the anthraflavone obtained from 2-methylanthraquinone (Bohn, Abstr., 1910, i, 405).

4-*Ethylbenzophenone*-2′-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4Et$, separates in needles, m. p. 122°; it dissolves in concentrated sulphuric acid with a yellow coloration, changing to a reddish-brown on heating.

4-*Ethyldiphenylmethane*-2′-*carboxylic acid*, $CO_2H\cdot C_6H_4\cdot CH_2\cdot C_6H_4Et$, crystallises in colourless needles, m. p. 86°. Concentrated sulphuric acid rapidly converts it at the ordinary temperature into a mixture of 2-*ethylanthrone*-9 and 2-*ethylanthranol*-9. The desmotropic mixture consists of irregular, yellow crystals and yellow needles, m. p. 67—75°. When brominated in acetic acid and boiled with water, 2-*ethylanthraquinone* is obtained in yellow needles, m. p. 108°. It dissolves in sulphuric acid with a reddish-yellow coloration, becoming greenish-yellow when heated.

1-*Nitro*-2-*ethylanthraquinone* forms yellowish-brown needles or plates, m. p. 226°.

1-*Amino*-2-*ethylanthraquinone* is obtained on reduction in red needles, m. p. 153—154°.

1-*Iodo*-2-*ethylanthraquinone* crystallises in lustrous, small, yellowish-brown leaflets, m. p. 149°.

2 : 2′-*Diethyl*-1 : 1′-*dianthraquinonyl*,

$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_2Et\cdot C_6H_2Et<\genfrac{}{}{0pt}{}{CO}{CO}>C_6H_4,$$

prepared by heating the above iodo-compound with copper powder, crystallises in yellowish-brown prisms, m. p. 315°; in concentrated sulphuric acid it forms a yellow solution, which becomes violet red on heating.

8 : 16′-*Dimethylpyranthrone* was obtained amorphous, m. p. much above 300°. It gives yellow solutions with a green fluorescence; the sulphuric acid solution is violet. It gives a deep violet, alkaline vat, which dyes cotton brownish-yellow.

4-n-*Propylbenzophenone*-2′-*carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CO\cdot C_6H_4\cdot C_3H_7,$$

crystallises in colourless needles, m. p. 125—126°.

4-n-*Propyldiphenylmethane*-2′-*carboxylic acid*,

$$CO_2H\cdot C_6H_4\cdot CH_2\cdot C_6H_4\cdot C_3H_7,$$

forms slender needles, m. p. 80—81°.

The mixture of 2-n-*propylanthrone*-9 and 2-n-*propylanthranol*-9 is obtained in slender, yellow, microscopic needles, m. p. 60—61°, only partly soluble in dilute sodium hydroxide.

2-n-*Propylanthraquinone* forms yellow, slender needles, m. p. 96—99°, and dissolves in concentrated sulphuric acid with a reddish-yellow coloration.

1-*Nitro*-2-n-*propylanthraquinone* crystallises in yellow plates, m. p. 180°. 1-*Amino*-2-n-*propylanthraquinone* forms red, lancet-shaped crystals of metallic lustre, m. p. 172—173°.

1-*Iodo*-n-*propylanthraquinone* separates in lancet-shaped, lustrous, golden needles, m. p. 148—149°.

2:2'-*Di*-n-*propyl*-1:1'-*dianthraquinonyl* has m. p. 214—215°; the solution in concentrated sulphuric acid is brown, becoming dark green at about 80° and violet-red at about 220°.

8:16-*Diethylpyranthrone* is a yellowish-brown powder more soluble than the dimethyl homologue. The coloration with concentrated sulphuric acid is blue. It gives a deep reddish-violet alkaline vat, and dyes lighter shades than pyranthrone.

[With E. Böcker.]—4-iso*Propylbenzophenone*-2'-*carboxylic acid* forms lustrous, silky needles, m. p. 133—134°.

4-iso*Propyldiphenylmethane*-2'-*carboxylic acid* crystallises in platelets, m. p. 111°.

The condensation product, 2-iso*propylanthrone*-9, was not isolated, but converted into 2-iso*propylanthraquinone*, which sublimes in concentrically grouped, yellow needles, m. p. 44—45°.

1-*Nitro*-2-iso*propylanthraquinone* forms yellow plates, m. p. 210—211°. 1-*Amino*-2-iso*propylanthraquinone* separates in red platelets or in needles with a green surface reflex, m. p. 146°.

1-*Iodo*-2-iso*propylanthraquinone* crystallises in well-formed bunches of yellow needles, m. p. 133—134°.

2:2'-*Di*-iso*propyl*-1:1'-*dianthraquinonyl* forms rhombohedric crystals, m. p. 326°. E. F. A.

Oxy-2-methylthiophens. Maurice Lanfry (*Compt. rend.*, 1911, 153, 821—823).—The action of hydrogen peroxide on 2-methylthiophen is similar to that on thiophen (this vol., i, 740), and the products closely resemble those previously obtained, the oxygen being united to sulphur. *Dioxy-2-methylthiophen*, $C_5H_6O_2S$, has b. p. 168—170°/760 mm., D^{13} 1·25. *Tetraoxy-2-methylthiophen*, $C_5H_6O_4S$, has b. p. 187—189°/760 mm., D^{13} 1·37; on treatment with excess of bromine it forms *tribromotetraoxy-2-methylthiophen tetrabromide*, $C_5H_3O_4Br_3S,Br_4$, a yellow substance, m. p. −8°, decomposing on distillation. Fuming nitric acid converts the oxymethylthiophens into an ill-defined, yellow *polynitro*-derivative.

Excess of hydrogen peroxide converts 2-methylthiophen into a brown, amorphous substance. W. O. W.

Preparation of Amino- and Alkylamino-substituted (in the Aryl Group) Derivatives of 3-Oxy-(1)-thionaphthen-2-carboxylic Acids and of 3-Oxy-(1)-thionaphthen. Kalle & Co. (D.R.-P. 237395).—When the *N*-substitution products of arylthio-

glycol-*o*-carboxylic acids (such as amino-, acylamino-, or alkylamino-acids) are fused with alkali hydroxides at about 170°, the fusion treated with water, and oxidised with potassium ferricyanide (or air), they furnish derivatives of "thioindigo."

3-Acetylamino-6-carboxyphenylthiolacetic acid,

$$NHAc\cdot C_6H_3(CO_2H)\cdot S\cdot CH_2\cdot CO_2H,$$

a yellow powder, is prepared from monoacetyl-2 : 4-diaminobenzoic acid by successive diazotisation, xanthogenation, and treatment with chloroacetic acid; on fusion with sodium hydroxide it yields 6-*amino-3-keto-(1)-thionaphthen-2-carboxylic acid*, a grey, crystalline powder, which on boiling with hydrochloric acid furnishes 6-*amino-3-keto-(1)-thionaphthen*, a crystalline powder, and this by oxidation is finally converted into an "aminothioindigo" derivative.

4-Acetylamino-6-carboxyphenylthiolacetic acid, prepared in a similar manner from monoacetyl-2 : 5-diaminobenzoic acid, successively yielded *5-amino-3-keto-(1)-thionaphthen-2-carboxylic acid*, *5-amino-3-keto-(1)-thionaphthen*, yellow needles, and, finally, "*pp*-diaminothioindigo" in black flakes.

F. M. G. M.

Anthraquinone-thioxanthone. Fritz Ullmann and Ernst Knecht (*Ber.*, 1911, **44**, 3125—3132. Compare Abstr., 1910, i, 270).—The colour change produced by the substitution of -S- for -NH- in the anthraquinoneacridones has been studied. Generally the result is the shifting of the colour into the yellow; thus the red anthraquinone-2 : 1-acridone corresponds with an orange anthraquinone-2 : 1-thioxanthone, and the isomeric orange 1 : 2-acridone compound corresponds with the yellow thioxanthone derivative.

Anthraquinone-*o*-thiolbenzoic acids were prepared by interaction of the appropriate chloro-derivatives with *o*-thiolbenzoic acid, and the former condensed by means of the *p*-toluenesulphonyl chloride or phosphorus pentachloride into anthraquinone-thioxanthones.

Anthraquinone-1-o-thiolbenzoic acid, $C_6H_4<^{CO}_{CO}>C_6H_3\cdot S\cdot C_6H_4\cdot CO_2H$, crystallises in orange-yellow plates, m. p. 261° (corr.).

Anthraquinone-2 : 1-thioxanthone, $C_6H_4<^{CO}_{CO}>C_6H_2<^{S}_{CO}>C_6H_4$, forms lustrous, orange-red platelets, m. p. 346° (corr.). The solution in concentrated sulphuric acid is red.

Anthraquinone-2-*o*-thiolbenzoic acid has m. p. 278° (corr.), and not 271° as previously stated (*loc. cit.*). Anthraquinone-1 : 2-thioxanthone forms small, yellow needles, m. p. 278° (corr.); the azine crystallises in yellow, lustrous platelets.

1 : 5-*Dichloroanthraquinone* forms citron-yellow needles, m. p. 251° (corr.). It condenses very readily with *o*-thiolbenzoic acid to *anthraquinone-1 : 5-bis-o-thiolbenzoic acid*,

$$CO_2H\cdot C_6H_4\cdot S\cdot C_6H_3<^{CO}_{CO}>C_6H_3\cdot S\cdot C_6H_4\cdot CO_2H,$$

which crystallises in sealing-wax-red needles, m. p. 349° (corr.). It dissolves in alkali with an orange-red, and in concentrated sulphuric acid with a Bordeaux-red, coloration.

Anthraquinone-2 : 1 : 6 : 5-*bisthioxanthone*,

$$C_6H_4<\underset{S}{\overset{CO}{}}>C_6H_2<\underset{CO}{\overset{CO}{}}>C_6H_2<\underset{S}{\overset{CO}{}}>C_6H_4,$$

forms red, lustrous platelets, which are not melted at 360°; they dissolve in concentrated sulphuric acid with a wine-red coloration.

1 : 8-*Dichloroanthraquinone* separates in yellow needles, m. p. 202°.

Anthraquinone-1 : 8-*bis-o-thiolbenzoic acid* forms orange-red crystals, m. p. 279° (corr.).

Anthraquinone-2 : 1 : 7 : 8-*bisthioxanthone* crystallises in Bordeaux-red, lustrous needles, giving a violet-red solution in concentrated sulphuric acid.

E. F. A.

Preparation of Diglycollic Esters of Quinine. C. F. BOEHRINGER & SÖHNE (D.R.-P. 237450).—*Quinine diglycollate*,

$$O(CH_2 \cdot CO_2 \cdot C_{20}H_{23}ON_2)_2,$$

is prepared by treating a chloroform solution of quinine (11 parts) with diglycollic acid (3 parts) and allowing the mixture to remain during several days. It is a voluminous, tasteless, colourless powder, m. p. 70° (about), sparingly soluble in water, readily so in organic solvents.

Quinine diglycollyl sulphate, $C_4H_4O_3(C_{20}H_{23}O_2N_2)_2,H_2SO_4,3H_2O$, is obtained in crystalline form by treating a dichloroethylene solution of quinine with diglycollyl chloride in the same solvent and subsequently adding dilute sulphuric acid; the ester separates on the addition of sodium acetate.

The Grignard reaction with magnesium ethyl bromide, quinine, and diglycollic acid can also be employed for this preparation.

F. M. G. M.

Rearrangement of Quinine by Sulphuric Acid. BRUNO BÖTTCHER and STEFANIE HOROWITZ (*Monatsh.*, 1911, 32, 793—796).—When quinine is heated at 100° with sulphuric acid, D 1·61, two bases, *A* and *B*, are formed; the former yields a soluble oxalate and sparingly soluble tartrate; the latter yields a sparingly soluble oxalate and a soluble tartrate.

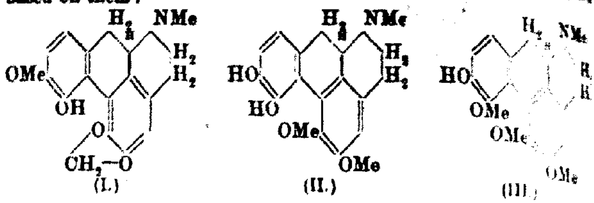
Base *A* crystallises in needles, m. p. 193·5° (corr.), $[\alpha]_D$ $-237·89°$; the solution in sulphuric acid fluoresces blue. The *sulphate* crystallises in bunches of needles, $[\alpha]_D$ $-234·5°$.

Base *B* forms colourless needles, m. p. 189° (corr.), $[\alpha]_D$ $-181·67°$; it is probably identical with Lippmann's *iso*quinine (Abstr., 1892, 82)

E. F. A.

Corydalis Alkaloids. IX. Corytuberine Sub-group. JOHANNES GADAMER (*Arch. Pharm.*, 1911, 249, 503—510. Compare Abstr., 1902, i, 391; this vol., i, 483, and following abstract).—The author has undertaken with FRITZ KUNTZE a revision of the chemistry of the alkaloids forming this sub-group. The experimental results of this work, which will be published later, are discussed, and the following constitutional

formulæ for bulbocapnine (I), corytuberine (II), and corydine (III) as based on them:



*iso*Corydine differs from corydine (III) only in the interchange of positions between –OMe and –OH in positions 3 and 4 in the phenanthrene nucleus. These formulæ are mainly based on the fact that in certain reactions these alkaloids show great similarity to *apo*morphine. Glaucine is the dimethyl ether of corytuberine (II). The two –OH groups in corytuberine are regarded as occupying positions 3 and 4, because (1) this alkaloid is readily oxidised by air in alkaline solutions, forming a dark green liquid. (2) The two hydroxyl groups in *apo*morphine occupy positions 3 and 4 in the phenanthrene nucleus, and the physiological action of corytuberine is very similar to that of *apo*morphine, whilst the characteristic emetic action disappears on methylation of these groups, as in bulbocapnine and corydine. (3) Bulbocapnine and *iso*corydine, like *apo*morphine, give Pellagri's reaction, so that they must contain a hydroxyl group in a position analogous to one of those in *apo*morphine, and as *iso*corydine is produced by methylation of corytuberine, the latter must also contain an –OH group similarly situated. Corytuberine itself does not give Pellagri's reaction, probably because it forms a betaine, in which the –OH group, which should function in Pellagri's reaction, is not available. T. A. H.

Corydalis Alkaloids. X. Bulbocapnine. JOHANNES GADAMER and FRITZ KUNTZE (*Arch. Pharm.*, 1911, **249**, 598–637. Compare Freund and Josephi, Abstr., 1894, i, 100; Herzig and Meyer, Abstr., 1898, i, 53, 389; Ziegenbein, Abstr., 1897, i, 175; Gadamer, Ziegenbein, and Wagner, Abstr., 1902, i, 391).—A historical résumé of work on bulbocapnine is first given, followed by a summary of the results and analogies on which the new formula for bulbocapnine is based (preceding abstract).

In the mother liquors from the preparation of bulbocapnine, dehydrocorydaline was obtained (compare Schmidt, Abstr., 1909, ii, 85). On methylation with methyl sulphate or diazomethane, bulbocapnine yields a monomethyl ether, $C_{20}H_{21}O_4N$, m. p. 130–131°, $[\alpha]_D^{20}$ + 247·2° in chloroform, forming hemihedral, tetragonal crystals $[a:c = 1:1·0554]$, which gives a crystalline *sulphate*, $B_2,H_2SO_4,7H_2O$. On oxidation with iodine in alcohol this gives *dehydrobulbocapnine methyl ether hydriodide*, $C_{20}H_{18}O_4NI$, m. p. 228°, which with gold chloride gives the *aurichloride*, $C_{20}H_{17}O_4N,HAuCl_4$, crystallising in slender, cinnamon-brown needles, and on reduction with zinc dust in dilute sulphuric acid gives dl-*bulbocapnine methyl ether*, m. p. 136°,

forming rhombic crystals [$a:b:c = 0.87288:1:0.61037$]. The latter on fractional crystallisation of the *d*-acid tartrate is separated into the optically isomeric methyl ethers.

On treatment with hot acetic anhydride, bulbocapnine yields a weakly basic diacetyl derivative, $C_{19}H_{17}O_4NAc_2$, which crystallises with ½ mol. $C_2H_5\cdot OH$, a fact which explains Ziegenbein's assumption that this product is a triacetyl derivative (*loc. cit.*). On warming with potassium hydroxide in alcohol, this yields the *potassium* derivative of N-*acetylbulbocapnine* as a yellow, crystalline precipitate, which rapidly becomes brown in the air, and with alcohol and dilute sulphuric acid gives N-*acetylbulbocapnine*, m. p. 163—165°, crystallising in slender, red needles. With benzoyl chloride, by the Schotten-Baumann method, bulbocapnine gives a weakly basic *monobenzoyl* derivative, m. p. 202—203°, $[a]_D^{20}$ + 92·7°, rhombic crystals [$a:b:c = 0.59437:1:0.63116$], which forms a *methiodide*, m. p. 228—230° (decomp.), $[a]_D^{20}$ + 28·1°, crystallising in rosettes of needles or silky leaflets, and on oxidation with iodine in alcohol gives *benzoyl-dehydrobulbocapnine hydriodide*, m. p. 219° (decomp.), $[a]_D = 0°$. The latter on reduction with zinc dust and sulphuric acid gives dl-*mono-benzoylbulbocapnine*, m. p. 201—202°, and this on hydrolysis yields dl-*bulbocapnine*, m. p. 209—210°, which can be separated into its optical isomerides by crystallisation of the *d*-acid tartrate. With hot benzoyl chloride, bulbocapnine gives a *dibenzoyl* derivative, m. p. 156—157°, $[a]_D = 0°$, which on treatment with sodium hydroxide in methyl alcohol yields N-*benzoylbulbocapnine*, m. p. 160°. Oxidation of dibenzoylbulbocapnine with chromic acid did not give a crystalline quinonoid derivative such as is obtained with tribenzoyl*apo*morphine, although the red substance produced is probably a quinone.

With methyl iodide, bulbocapnine gives a methiodide (Freund and Josephi and Ziegenbein, *loc. cit.*), $[a]_D^{20}$ +173·8° in alcohol, and the methyl ether on treatment with methyl iodide yields *bulbocapnine methyl ether methiodide*, $C_{20}H_{21}O_4N\cdot MeI$, m. p. 245—247°, $[a]_D^{20}$ +163·7°.

Dimethylbulbocapnimethine, $C_{17}H_{13}O_4\cdot CH_2\cdot CH_2\cdot NMe_2$, best obtained by the method described by Pschorr for the analogous *apo*morphine compound (Abstr., 1906, i, 878), is a viscid, yellow liquid and is optically inactive; it furnishes an unstable *methiodide*,

$$C_{17}H_{13}O_4\cdot CH_2\cdot CH_2\cdot NMe_3I.$$

and a *methosulphate*, crystallising in thick, yellow needles. Either of these on warming with sodium hydroxide in methyl alcohol furnishes 3:4-*dimethoxy*-5:6-*methylenedioxy*-8-*vinylphenanthrene*, m. p. 101°, crystallising from ether in small, yellow needles. This on distillation with zinc dust gives ethylphenanthrene, which could not be obtained pure, but furnished a picrate, m. p. 138—140° (compare Pschorr, Abstr., 1906, i, 178), and on oxidation with permanganate in acetone yields the corresponding 3:4-*dimethoxy*-5:6-*methylenedioxy-phenanthrene*-8-*carboxylic acid*, m. p. 228°, which crystallises in slightly red needles. The latter on further oxidation with permanganate in water gives (1) a soft mass, and (2) a *substance*, m. p. 247°, crystallising in red needles, which is probably dimethoxymethylene-dioxyphenanthraquinonecarboxylic acid; it dissolved in alkalis,

forming eventually a colourless solution, from which acids liberate a colourless *substance*, m. p. 256—257°, which gradually becomes yellow on exposure to light. The soft mass referred to above, on solution in alcohol, deposits after a time a crystalline *substance*, m. p. 209°.

T. A. H.

Alkaloids of Ipecacuanha Root. Oskar Keller (*Arch. Pharm.*, 1911, 249, 512—524. Compare Paul and Cownley, Abstr., 1896, i, 192; Frerichs and Tapis, Abstr., 1902, ii, 711).—The bark of the root was extracted with ether, then moistened with ammonia solution, and re-extracted with ether and finally with chloroform. The first operation gave no alkaloid. The second furnished cephaëline and emetine, and the third psychotrine. Cephaëline crystallised from the second ethereal extract on concentration, and emetine was recovered from the mother liquors. Carthagena root yielded more cephaëline than Rio root. The colour reactions of both alkaloids are given (compare Allen and Scott-Smith, Abstr., 1903, ii, 117), and the dilutions at which they cease to be precipitated by the usual reagents.

Cephaëline softens at 93°, melts at 104—105°, and is readily soluble in alcohol or chloroform, less so in ether or light petroleum.

Emetine, $C_{30}H_{44}O_4N_2$, was obtained as a snow-white, amorphous powder; the *hydrochloride*, $B,2HCl,3H_2O$, crystallised in groups of needles and melted indefinitely, the *hydrobromide*, B,2HBr, in minute needles, and the *hydriodide*, $B,2HI,2H_2O$, m. p. 228—230°, in small masses of needles; the platinichloride, m. p. 248—249°, is amorphous. Emetine furnishes a *dibenzoyl* derivative, m. p. 96—106°, in which one benzoyl group is probably attached to a second nitrogen atom. It contains two methoxyl groups, and on heating with methyl iodide and sodium hydroxide forms a *methyl dimethiodide*, so that it appears to contain both a secondary and a tertiary nitrogen atom.

T. A. H.

Methyl Ether of Codeine and its Behaviour on Exhaustive Methylation. Morphine. XII. Ludwig Knorr and Paul Roth (*Ber.*, 1911, 44, 2754—2758).—When α-chlorocodeide is heated in an autoclave for two days at 100—110° with sodium methoxide in methyl-alcoholic solution, codeine methyl ether is formed, and can be isolated as *hydrochloride*, $C_{19}H_{23}O_3N,HCl$, which crystallises (with ½ mol. of alcohol) in needles, m. p. about 285° (previously sintering); $[\alpha]_D^{20}$ − 66° (in water). The *hydriodide*, $C_{19}H_{23}O_3N,HI$, crystallises in rosettes of needles, m. p. about 238—240° (decomp.). The *sulphate* (m. p. 241°), and the *nitrate* (which decomposes at 219°) also crystallise well. *Codeine methyl ether*, obtained from its salts, is a well crystalline substance, m. p. 137°, $[\alpha]_D^{15}$ − 80° (in alcohol, $c = 1.965$). The *methiodide*, $C_{19}H_{23}O_3N,MeI$, crystallises in compact prisms, m. p. 270° (decomp.).

The methiodide, when boiled with sodium hydroxide, yields quantitatively a *methine base*, which is not crystalline; it suffers no rearrangement when heated with alcoholic potassium hydroxide (com-

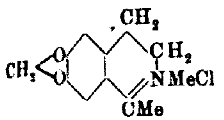
…are Knorr, Hörlein, and Grimme, Abstr., 1907, i, 956). The …hydriodide (methylmorphimethine methyl ether hydriodide),

$$C_{20}H_{25}O_3N\cdot HI,$$

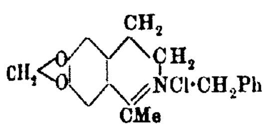
crystallises in needles or plates, m. p. about 204—208° (sintering from 200°), $[\alpha]_D$ −85·5° (c = 1·4035) or −87·3° (c = 1·4950). The *methiodide*, $C_{20}H_{25}O_3N\cdot MeI$, forms feathery crystals, m. p. 275°.

Methylmorphimethine methyl ether methiodide was deprived of iodine by means of silver oxide, and the resulting quaternary base was heated at 150° in a stream of hydrogen. Complete decomposition took place, and the following products were isolated and identified: ethylene, methylmorphenol, methyl alcohol, trimethylamine. R. V. S.

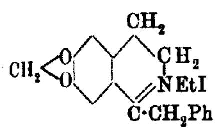
Preparation of 1-Aryl, Alkyl, or Alkylaryl Substituted Hydrastinines. FARBENFABRIKEN VORM. FRIEDR. BAYER & Co. (D.R.-P. 235358. Compare Abstr., 1908, i, 901; this vol., i, 906).—When N-acyl derivatives of homopiperonylamines are submitted to the action of condensing agents, they furnish hydrastinine derivatives. When *acetylhomopiperonylamine*, $CH_2{:}O_2{:}C_6H_3\cdot CH_2\cdot CH_2\cdot NHAc$, colourless leaflets, m. p. 101°, is boiled with phosphoric oxide in toluene solution, it yields 6 : 7-*methylenedioxy*-1-*methyl*-3 : 4-*dihydro*iso*quinoline*; its *picrate*, a yellow, crystalline powder, has m. p. 232°; and the *methiodide*, yellow leaflets, m. p. 257°; when shaken during several hours with freshly precipitated silver chloride, it furnishes 1-*methylhydrastinine hydrochloride* (formula I), feathery needles, m. p. 232°.



(I.)



(II.)



(III.)

When the foregoing *iso*quinoline derivative is treated with benzyl chloride it yields 2-*chloro*-6 : 7-*methylenedioxy*-2-*benzyl*-1-*methyl*-3 : 4-*dihydro*iso*quinoline* (formula II), yellowish-brown needles, m. p. 248°.

Phenacetylhomopiperonylamine, $CH_2{:}O_2{:}C_6H_3\cdot[CH_2]_2\cdot NH\cdot CO\cdot CH_2Ph$, yellow needles, m. p. 96°, under similar treatment yields 6 : 7-*methylenedioxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, a yellow, oily liquid, b. p. 240°/16 mm.; its *picrate*, yellow crystals, has m. p. 189—190°, and the *methiodide*, yellow needles, m. p. 252°, on treatment with silver chloride furnishes 1-*benzylhydrastinine hydrochloride* (or *methochloride*), an uncrystallisable resin, readily soluble in water.

6 : 7 - *Methylenedioxy* - 1 - *benzyl*-3 : 4-*dihydro*iso*quinoline ethiodide* (formula III) forms yellow crystals, m. p. 214°.

Benzoylhomopiperonylamine, m. p. 122°, yields 6 : 7-*methylenedioxy*-1-*phenyl*-3 : 4-*dihydro*iso*quinoline*, colourless crystals, m. p. 142—143°; its *methiodide*, yellow needles, has m. p. 241°. F. M. G. M.

Strychnine and Brucine. [III.] ROBERTO CIUSA and G. SCAGLIARINI (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 201—205. Compare Abstr., 1910, i, 583; this vol., i, 155).—By the action of bromine on strychnine, under the conditions employed by Löbisch and Schoop (Abstr., 1886, 267), the authors obtained a monobromostrychnine, m. p. 222—223°, identical with that formerly described by them; they consider, therefore, that the *β*-monobromostrychnine of Löbisch and Schoop does not exist.

When treated with bromine in glacial acetic acid, brucine yields a *perbromide*, $C_{23}H_{26}O_4N_2Br_3,H_2O$, crystallising in yellowish-white needles, which do not melt at 270°. From it a *monobromostrychnine platinichloride*, $(C_{23}H_{25}O_4N_2Br)_2,H_2PtCl_6,H_2O$, can be obtained.

On treating strychnine with potassium chlorate and hydrochloric acid in the cold, the tetrachlorostrychnine of Minunni and Ortoleva (Abstr., 1900, i, 309) is produced, together with an amorphous, isomeric *tetrachlorostrychnine*, $C_{21}H_{18}O_2N_2Cl_4,HCl,2H_2O$. When the cooling is omitted in the above reaction, an *octachlorostrychnine* is obtained as a yellowish-white, crystalline powder, which on analysis gives numbers corresponding approximately with the formula

$$C_{24}H_{14}O_2N_2Cl_8,3H_2O.$$

It yields a p-*nitrophenylhydrazone*, to which the formula

$$C_{24}H_{14}ON_2Cl_8{:}N_2H{\cdot}C_6H_4{\cdot}NO_2,3H_2O,$$

is ascribed.

The physiological action of the derivatives now and previously described has also been studied. The two dibromides, m. p. 122 and 260°, bromostrychnine, and the corresponding dibromide are as toxic as strychnine itself, whilst the octachlorostrychnine (like Minunni's tetrachlorostrychnine) and the acid, $C_{19}H_{22}O_6N_2$, are not toxic. R. V. S.

Iodine Derivatives of Strychnine, Brucine, and Some Other Alkaloids. L. KRAUZE (*Bull. Acad. Sci. Cracow*, 1911, [A], **6**, 355—368).—True periodides of strychnine bases have been obtained by Buraczewski and Kozniewski (Abstr., 1908, i, 1007) and Kozniewski (Abstr., 1909, i, 826).

When more iodine is used, under otherwise similar experimental conditions, two modifications of a *strychnine heptaiodide*,

$$C_{21}H_{22}O_2N_2,HI,I_6,$$

are formed. One of these is obtained from solutions containing 10% excess of iodine in brownish-needles with a golden lustre, m. p. 151°; it soon decomposes when kept. The other is formed when considerably more iodine is used; it separates in hard, black prisms of a steel-like lustre, m. p. 176—177°, which are stable when kept. Both forms when warmed with alcohol or acetone are converted into Jörgensen's tri-iodide (*J. pr. Chem.*, 1870, [ii], **2**, 1334).

By the action of an alcoholic iodine solution on di-iodostrychnine, a brown product is obtained containing more than three iodine atoms, which is a mixture, and could not be obtained crystalline. On warming with acetone, it becomes yellow, forming a new insoluble

...iodostrychnine. Strychnine evidently tends to form several periodides, a property entirely lacking in brucine.

Baraczewski and Dziurzyński (Abstr., 1910, i, 873) have shown that complicated reactions take place on boiling di-iodostrychnine in acetone; two non-poisonous, crystalline products were obtained. These have now been studied more fully. The one forms small, silky needles, m. p. 281°, $C_{24}H_{27}O_3N_2I,1\frac{1}{2}H_2O$, the other yields hard prisms, m. p. 271°, $C_{24}H_{29}O_4N_2I,1H_2O$.

The former, *iodo-acetonylstrychnine*, $C_{21}H_{22}O_2NI{\cdot}CH_2{\cdot}COMe$, does not interact with acids or alkalis; with moist silver oxide a soluble, easily decomposed base is obtained; it reduces Fehling's solution and forms a *phenylhydrazone*, which is not well characterised. The *nitrate* forms lustrous, yellow, silky needles; the *dichromate* is yellow and flocculent. It is optically inactive and does not react with methyl iodide.

The second substance, *iodoacetonylstrychnic acid*,

$$NH{:}C_{20}H_{22}O(CO_2H){:}NI{\cdot}CH_2{\cdot}COMe,$$

when dried in a vacuum loses half a molecule of water, forming an *anhydro acid*, $(C_{24}H_{28}O_3N_2I)_2O$. It forms salts with salts of the heavy metals; with potassium dichromate a yellow, flocculent precipitate, $(C_{24}H_{29}O_4N_2)Cr_2O_7$, is obtained. The *picrate*, $C_{30}H_{31}O_{11}N_5$, is yellow. It reduces Fehling's solution, and forms a *phenylhydrazone*, m. p. 124°. With sodium nitrite in acid solution a crystalline precipitate of the nitrosoamine sulphate is formed.

With alkaline methyl-alcoholic methyl iodide, *iodoacetonyl-N-methylstrychnic acid*, $C_{25}H_{31}O_4N_2I$, is obtained; it crystallises in needles, m. p. 248°.

Analogous compounds could not be obtained from other alkaloids. Di-iodobrucine and acetone interact to give a *periodide*,

$$C_{23}H_{26}O_4N_2,HI,I_2,$$

crystallising in short, hard, brownish-red columns, m. p. 260°.

From di-iodocinchonine or di-iodoquinidine and acetone, the hydriodides of the bases were obtained. E. F. A.

Reduction Catalysts. V. Hydrogenation of Alkaloids. Aladar Skita and H. H. Franck (*Ber.*, 1911, **44**, 2862—2867).—Strychnine in dilute acetic acid containing a little 1% palladium chloride and 1% gum arabic is reduced in hydrogen under a pressure of 2 atmospheres at the ordinary temperature to *dihydrostrychnine*, $C_{21}H_{24}O_2N_2$, m. p. 209—210°, whilst brucine is converted into *dihydrobrucine*, $C_{23}H_{28}O_4N_2$, m. p. 115°, under similar conditions; under a pressure of 3 atmospheres at 70°, dihydrostrychnine is reduced further to Tafel's tetrahydrostrychnine.

In hydrochloric acid solution containing a little palladium chloride (or platinic chloride), morphine, codeine, quinine, and cinchonine are reduced by hydrogen to dihydromorphine (Oldenberg, this vol., i, 668), *dihydrocodeine*, $C_{18}H_{23}O_3N$, m. p. 65°, dihydroquinine, and dihydrocinchonine respectively, whilst piperine is converted into *tetrahydropiperine*, b. p. 261°/14 mm. These last reductions are not effected by the colloidal metal. C. S.

Strychnine Alkaloids. XII. Derivatives of Bisapomethylbrucine. HERMANN LEUCHS and RUDOLPH ANDERSON (*Ber.*, 1911, 44, 3040—3049. Compare this vol., i, 746).—The *nitrate*,

$$C_{21}H_{21}O_4N_2,HNO_3,1\frac{1}{2}H_2O,$$

hydrobromide, $C_{21}H_{22}O_4N_2,HBr,2H_2O$, *zincichloride*,

$$C_{21}H_{22}O_4N_2,H_2ZnCl_4,H_2O,$$

diacetyl derivative, $C_{25}H_{26}O_6N_2$, m. p. 232—233°, and the *methiodide*, m. p. 280° (decomp.), of bis*apo*methylbrucine are described. The action of concentrated nitric acid at −5° on bis*apo*methylbrucine yields *nitrobisapomethyldehydrobrucine nitrate*,

$$C_{21}H_{19}O_6N_3,HNO_3,3H_2O,$$

orange needles, which is converted by warm 10% nitric acid into cacotheline. The latter is obtained directly by warming bis*apo*methylbrucine hydrochloride with 10% nitric acid.

An attempt to regenerate brucine from bis*apo*methylbrucine by means of methyl iodide failed. However, with a large excess of methyl sulphate, bis*apo*methylbrucine hydrochloride in alkaline solution yields *brucine methosulphate*, $C_{23}H_{26}O_4N_2,Me_2SO_4,2\frac{1}{2}H_2O$, m. p. 268° (decomp.), which crystallises in three forms, has a very bitter taste, and responds to the red brucine reaction. This substance, which is identical with that obtained from methyl sulphate and brucine itself, is converted by warm aqueous sodium hydroxide into methylbrucine, the *acetyl* derivative of which has m. p. 157—158° after strongly sintering at about 120° and resolidifying. When boiled with 10% nitric acid, methylbrucine yields *cacotheline methonitrate*, $C_{21}H_{21}O_7N_3,MeNO_3,2H_2O$, orange plates, which carbonises at about 280°. C. S.

Strychnine Alkaloids. XIII. Isolation of a Fourth Brucinesulphonic Acid. HERMANN LEUCHS and WALTER GEIGER (*Ber.*, 1911, 44, 3049—3051).—When brucine is sulphonated by manganese dioxide and sulphurous acid in the manner described previously (Abstr., 1908, i, 563; 1909, i, 120, 253, 602, 671), and the resulting sulphonic acids are extracted with water, a very small amount (3%) of a very sparingly soluble *brucinesulphonic acid*, $C_{23}H_{28}O_7N_2S,4H_2O$, is left undissolved. This acid crystallises in large, truncated prisms, has $[\alpha]_D^{20}$ −122·2° in N/10-alkali, and is soluble in 170 parts of boiling water. C. S.

Tetrahydropiperine and Tetrahydropiperic Acid. WALTHER BORSCHE (*Ber.*, 1911, 44, 2942—2945. Compare this vol., i, 860).—β-Styrylacrylic acid is readily reduced by palladium and hydrogen to δ-phenylvaleric acid, and the same method applied to piperine furnishes a quantitative yield of tetrahydropiperine, which on hydrolysis gives piperidine and tetrahydropiperic acid. The latter crystallises from dilute alcohol in colourless leaflets, m. p. 100—101° (compare Buri, Abstr., 1883, 485). The *methyl* ester, b. p. 193—195° is a colourless, odourless oil. The *acid chloride* is a mobile oil, and on distillation decomposes, giving (1) a brown, resinous residue, which evolves hydrogen chloride, and (2) a viscid, colourless liquid, which deposits crystals. The *amide*, m. p. 110°, prepared from the chloride

rystallises in glancing leaflets. The chloride on treatment with luminium chloride in carbon disulphide gives *methylenedioxybenzosuberone*, $\begin{matrix}CH_2\text{——}CO\\CH_2\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2$, as a nearly colourless oil, ielding a *semicarbazone*, m. p. 238—239° (decomp.), crystallising in mall, colourless needles. T. A. H.

Synthesis of 2 : 4-Dimethyl-3-ethylpyrrole, a Contribution o the Question of the Constitution of Hæmopyrrole. Ludwig Knorr and Kurt Hess (*Ber.*, 1911, 44, 2758—2767).—According to Piloty (this vol., i, 92), hæmopyrrole is 2 : 4-dimethyl-3-ethylpyrrole, whilst phonopyrrole is 2 : 3-dimethyl-4-ethylpyrrole, but the synthesis of these substances has not yet been accomplished. The present authors have prepared 2 : 4-dimethyl-3-ethylpyrrole from 3-acetyl-2 : 4-dimethylpyrrole, obtained from the ethyl carboxylate produced by combination of nitrosoacetoacetic ester with acetylacetone. The synthetic product is similar to, but not identical with, hæmopyrrole, which must be 2 : 3-dimethyl-4-ethylpyrrole, therefore, in view of Piloty's work. The identity of 2 : 4-dimethyl-3-ethylpyrrole with phonopyrrole remains to be established, owing to the lack of crystalline derivatives of the latter substance. 2 : 3 : 5-Trimethylpyrrole (compare Ciamician and Dennstedt, *Ber.*, 1881, 14, 1340), 2 : 5-dimethyl-3-ethylpyrrole, and 2 : 5-dimethyl-3-propylpyrrole are also described.

The preparation of the pyrrole derivatives from the oximinoketones and acetoacetic ester was effected by the method formerly described (Knorr, Abstr., 1887, 275). The saponification of the carboxylic esters was carried out with 10% alcoholic sodium hydroxide containing a little water. On heating, the carboxylic acids lose carbon dioxide, the reaction being conducted in an atmosphere of nitrogen or hydrogen.

Ethyl 2 : 3 : 5-*trimethylpyrrole*-4-*carboxylate*, $C_{10}H_{15}O_2N$ (by reduction of methyl oximinoethyl ketone and acetoacetic ester), crystallises in small needles, m. p. 104—105°. The *acid*, $C_8H_{11}O_2N$, decomposes at 198°. 2 : 3 : 5-*Trimethylpyrrole*, $C_7H_{11}N$, has b. p. 180—181°/754 mm. (corr.).

Ethyl 2 : 5-*dimethyl*-3-*ethylpyrrole*-4-*carboxylate*, $C_{11}H_{17}O_2N$ (from methyl oximinopropyl ketone and acetoacetic ester), crystallises in small needles, m. p. 106—107°. The *acid*, $C_9H_{13}O_2N$, decomposes at about 200°. 2 : 5-*Dimethyl*-3-*ethylpyrrole*, $C_8H_{13}N$, has b. p. 187—188°/759 mm. (corr.), 93—94°/21 mm. It shows the pine splinter reaction, and gives a white precipitate with mercuric chloride, but differs from its isomerides in having an odour reminiscent of chloroform, and in being much less sensitive to oxygen.

Ethyl 2 : 5-*dimethyl*-3-*propylpyrrole*-4-*carboxylate*, $C_{12}H_{19}O_2N$ (from *nitrosobutyl methyl ketone*, which has m. p. 60°, and acetoacetic ester), forms prismatic crystals, m. p. 110°. The *acid*, $C_{10}H_{15}O_2N$, has m. p. about 210° (decomp.). 2 : 5-*Dimethyl*-3-*propylpyrrole*, $C_9H_{15}N$, has b. p. 206—207°/760 mm.

For the preparation of 2 : 4-dimethyl-3-ethylpyrrole another method had to be devised, advantage being taken of the fact (L. Wolff,

unpublished) that hydrazones can be reduced to hydrocarbons with sodium ethoxide. 3-*Acetyl-2 : 4-dimethylpyrrolehydrazone* (compare Knorr and Lange, Abstr., 1902, i, 821), $C_8H_{13}N_3$, forms rhombic crystals, m. p. 178—179°. When this substance is heated with an alcoholic solution of sodium ethoxide for fourteen hours at 150—160° in a sealed tube filled with nitrogen, 2 : *4-dimethyl-3-ethylpyrrole* is produced, and is isolated by distillation in steam, saturation of the distillate with ammonium sulphate, and extraction with ether, care being taken to conduct all the operations in an atmosphere of hydrogen. The distillation of the substance is carried out as indicated by Piloty (*loc. cit.*) for hæmopyrrole. 2 : 4-Dimethyl-3-ethylpyrrole, $C_8H_{13}N$, has b. p. 96°/16 mm., 107°/27 mm., 118°/37 mm. It behaves like hæmopyrrole towards nitrous acid, yielding methylethylmaleinimide, but is not fluorescent, and yields a *picrate* which forms compact crystals, m. p. 131—132° (hæmopyrrole picrate has m. p. 108°).

R. V. S.

Products from Pyrrole-2-carboxylic Acid. EMIL FISCHER and DONALD D. VAN SLYKE (*Ber.*, 1911, 44, 3166—3171).—Pyrrole-2-carboxylic acid, in spite of the sensitiveness of the pyrrole ring to acids, is relatively easily converted into the chloride by phosphorus pentachloride. The chloride affords a convenient material for the preparation of the ester, amide, and anilide of the acid; it has also been coupled with glycine to form 2-pyrroylglycine,

$$CH<\begin{matrix}CH:C\cdot CO\cdot NH\cdot CH_2\cdot CO_2H\\ CH\cdot NH\end{matrix}.$$

Pyrrole-2-carboxylic acid shows a very marked red coloration in aqueous or alcoholic solution with ferric chloride, and resembles in this respect the phenolcarboxylic acids.

a-Pyrrolecarboxyl chloride, $C_4H_4N\cdot COCl$, crystallises in long, yellow needles, aggregated in bunches, m. p. about 90°. When carefully purified, it forms very long, colourless crystals, which sinter at 110° and subsequently blacken without melting.

Pyrrole-2-carbanilide, prepared by interaction of pyrrolecarboxyl chloride and aniline in ethereal solution, forms colourless, long, and much intergrown prisms, m. p. 153—154° (corr.) after previous sintering.

a-Pyrroylglycine ethyl ester crystallises in six-sided platelets, m. p. 118° (corr.). *a-Pyrroylglycine* forms small, spindle-shaped crystals, m. p. 167° (corr.). It gives no coloration with ferric chloride.

E. F. A.

Action of Ammonia on Benzoyldehydracetic Acid. PAUL IW. PETRENKO-KRITSCHENKO and JOH. SCHÖTTLE (*Ber.*, 1911, 44, 2826—2830).—Feist's so-called 2 : 6-diphenyl-4-pyridone, obtained from benzoyldehydracetic acid and ammonia (Abstr., 1891, 45), is not identical with the author's compound of the same name (Abstr., 1909, i, 605), and is proved to be probably the *lactam*,

$$NH<\begin{matrix}CPh{=}CH\\ CO\cdot CHBz\end{matrix}>CO,$$

of benzoyldehydracetic acid by analysis, and by the fact that it is

verted by alcoholic potassium hydroxide into 3:6-*diphenyl-4-pyridone-3-carboxylic acid*, $NH<\begin{matrix}CPh{=\!=\!=}CH\\CPh:C(CO_2H)\end{matrix}>CO$, which yields 2:6-diphenyl-4-pyridone (m. p. 176—178°) at its m. p., 243—245°.

Feist's compound, which can also be converted into 2:6-diphenyl-pyridone hydrochloride by concentrated hydrochloric acid at 180°, is obtained from benzoyldehydracetic acid and alcoholic ammonia even at the ordinary temperature in two to three days (compare Feist, *loc. cit.*). C. S.

Toluoyl- and Xyloyl-picolinic Acids. OTTOKAR HALLA (*Monatsh.*, 1911, 32, 747—751).—Just (Abstr., 1898, i, 42) has obtained *p*-toluoylpicolinic acid by the condensation of quinolinic anhydride with toluene in presence of aluminium chloride. Quinolinic acid affords an exception to Kirpal's rule that two isomeric ketonic acids are formed in this reaction, as he only obtained 3-benzoylpicolinic acid on condensing it with benzene.

It is now found that when condensed with toluene, 3-*p*-toluoylpicolinic acid, m. p. 169°, is the main product, but that traces of a compound, m. p. 150°, are also formed; this has not been investigated. The 3-*p*-tolyl pyridyl ketone obtained by Just on heating 3-*p*-toluoylpicolinic acid at its melting point, has been synthesised from nicotinyl chloride and toluene; this establishes the formula of the 3-*p*-toluoylpicolinic acid, which has also been synthesised from quinolinic acid ethyl ester chloride and toluene.

3-(*m*:4)-*Xyloylpicolinic acid*, prepared in a similar manner from *m*-xylene, has m. p. 142°. On heating, β-*m*:4-*xylyl pyridyl ketone* is obtained, identical with that prepared from nicotinyl chloride and xylene; it is a faintly yellow-coloured oil, b. p. 240°, and forms a *picrate*, crystallising in yellow plates, m. p. 134°. E. F. A.

Aldehydes of Oxindole, Indoxyl, and Hydroxythionaphthen. PAUL FRIEDLÄNDER and ST. KIELBASINSKI (*Ber.*, 1911, 44, 3098—3108).—Friedländer and Schwenk (Abstr., 1910, i, 592) have shown that indigotin is decomposed by potassium hydroxide at 150° into anthranilic acid and indoxylaldehyde. In a similar manner the isomeric oxindolealdehyde, $C_6H_4<\begin{matrix}C(CHO)\\NH{-\!-\!-}\end{matrix}>C\cdot OH$, is obtained from "thioindigoscarlet R," whilst the dye prepared by condensing hydroxythionaphthen with *N*-methylisatin yields a *N*-methyl derivative of oxindolealdehyde, $C_6H_4<\begin{matrix}C(CHO)\\NMe{-\!-}\end{matrix}>C\cdot OH$. All three compounds show the normal aldehyde reactions.

Indoxylaldehyde, however, behaves abnormally towards mineral acids, which on moderate warming convert it into an intense violet dye; this dissolves in alkalis with a bluish-green coloration.

3-Indoxyl-2-thionaphthen-2′-one (Abstr., 1908, i, 673) is decomposed by alkali to 3-hydroxythionaphthen-2-aldehyde,

$$C_6H_4<\begin{matrix}C(OH)\\S{-\!-\!-\!-}\end{matrix}>C\cdot CHO\,;$$

this is converted quantitatively by dilute acids into a red dye dis-

solving in alkali with a bluish-violet coloration. This dye is also formed from equal molecules of hydroxythionaphthen and hydroxythionaphthenaldehyde, and has the constitution

$$C_6H_4{<}{}^{C(OH)}_{S\text{———}}{>}C\cdot CH:C{<}{}^{CO}_{S}{>}C_6H_4.$$

The same dye is formed from hydroxythionaphthen under a variety of conditions; for example, by the action of air on the strongly alkaline solution, particularly in presence of formaldehyde or other aliphatic aldehyde. It is also formed on heating carboxyphenylsulphoxideacetic acid, $CO_2H\cdot C_6H_4\cdot SO\cdot CH_2\cdot CO_2H$, in anhydrous potassium sodium acetate at 160—170°.

It is probable that the dye formation from indoxylaldehyde is similar in character, and that it may be formulated as

$$C_6H_4{<}{}^{C(OH)}_{NH\text{—}}{>}C\cdot CH:C{<}{}^{CO}_{NH}{>}C_6H_4.$$

Other analogous hydroxyaldehydes, for example, indandionealdehyde, $C_6H_4{<}{}^{C(OH)}_{CO\text{——}}{>}C\cdot CHO$, behave similarly towards acids.

The 3-aldehydes of oxindole and 2-hydroxythionaphthen are likewise sensitive towards mineral acids; the latter,

$$C_6H_4{<}{}^{C(CHO)}_{S\text{———}}{>}C\cdot OH,$$

is prepared by the action of potassium hydroxide on 2'-indoxyl-3-thionaphthen-2-one (*loc. cit.*).

Oxidole-3-aldehyde crystallises in faintly yellow-coloured needles, m. p. 213°; the aqueous solution is turned dark blue by ferric chloride. The *sodium* salt forms light grey crystals. The *phenylhydrazone* separates in stellar aggregates of pale yellow needles, m. p. 210°. The *aldazine* forms orange-yellow needles, m. p. 239°. The *oxime* forms corny crystals, m. p. 150°; its hydrochloride and sulphate crystallise well. The *anil* crystallises in yellow needles, m. p. 246° (decomp.). Analogous sparingly soluble anils are formed with *benzidine*, yellow needles, m. p. 300°, p-*toluidine*, greenish-yellow plates, m. p. 173°, m-*aminobenzoic acid*, yellow needles, m. p. above 290°, p-*phenylenediamine*, yellow plates, m. p. above 300°.

1-*Methyloxindole-3-aldehyde* crystallises in pale yellow needles, m. p. 186°; the *sodium* salt is sparingly soluble. The following derivatives are described: *phenylhydrazone*, broad, pale yellow needles, m. p. 193°; *oxime*, small, yellow, indefinitely formed needles, m. p. 111°; *aldazine*, orange-yellow needles, m. p. 211°; *anil*, pale yellow needles, m. p. 141°; *benzidine* derivative, greenish-yellow needles, m. p. 218°; p-*toluidine* derivative, well-formed, yellow needles, m. p. 150°; m-*aminobenzoic acid* derivative, yellow needles, m. p. 296°; p-*phenylenediamine* compound, orange-yellow needles, m. p. 210° (decomp.).

Indoxyl-2-aldehyde, m. p. 145°, forms a *phenylhydrazone*, crystallising in yellow needles, m. p. 116° (decomp.); the *aldazine* forms small, orange-red needles, decomp. above 150°; the *anil* gives orange-yellow needles, m. p. 195° (decomp.).

3-*Hydroxythionaphthen-2-aldehyde* crystallises in yellow needles, m. p. 107°, and gives a dark olive-green coloration with ferric chloride. The *phenylhydrazone* crystallises in broad, golden-yellow needles,

m. p. 137°. The *dye*, $C_{17}H_{10}O_2S_2$, obtained on warming with 5% sulphuric acid crystallises in large, red needles; the *sodium* salt forms lustrous, gold platelets. The corresponding *dye*, $C_{17}H_9O_2S_2Cl$, obtained on condensing hydroxythionaphthenaldehyde with 6-chlorohydroxythionaphthen, is very similar, crystallising in slender, red needles.

2-*Hydroxythionaphthen*-3-*aldehyde* crystallises in colourless needles, m. p. 126—127°; it gives a dark blue coloration with ferric chloride. The *aldazine* forms slender, yellow needles, m. p. 203°; with anthranilic acid a yellow, crystalline precipitate, m. p. 249°, of the *azomethine* is obtained. E. F. A.

Cyclic Ammonium Bases. HERMAN DECKER and ADOLF KAUFMANN (*J. pr. Chem.*, 1911, [ii], 84, 425—448. Compare this vol., i, 807).—An aqueous solution of *iso*quinoline methiodide, when treated with potassium hydroxide and shaken with benzene, yields the corresponding carbinol base (1-hydroxy-2-methyldihydro*iso*quinoline). By shaking the benzene solution with water, the greater part of the carbinol base may be extracted in the form of the ammonium base (2-methyl*iso*quinolinium hydroxide), the amount of which may be determined by titration with hydrochloric acid. The dilute aqueous solutions thus obtained are strongly alkaline, precipitate metallic hydroxides, and show all the characteristic properties of aqueous solutions of aliphatic ammonium bases. In contrast to the carbinol base, which undergoes atmospheric oxidation very readily, the ammonium base is very stable, its aqueous solutions showing no change even on exposure to air for seventy-two hours. Dilute aqueous solutions of the ammonium base, when shaken with benzene, yield no appreciable amount of the carbinol base; on the addition of sodium hydroxide, however, considerable quantities of the carbinol base may be extracted.

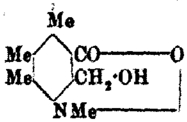
From these observations the conclusion is drawn that in aqueous solution there exists an equilibrium between the ammonium and carbinol bases: $C_6H_4<\begin{matrix}CH:CH\\ CH:NMe\cdot OH\end{matrix} \rightleftharpoons C_6H_4<\begin{matrix}CH{=\!=}CH\\ CH(OH)\cdot NMe\end{matrix}$; in dilute solution the amount of the latter base is very small, but increases on the addition of an alkali hydroxide.

2-*Methylisoquinolinium picrate*, $C_{16}H_{12}O_7N_4$, crystallises in long, slender, yellow needles, sintering at 183°, m. p. 187°.

Similar experiments were carried out with quinoline methiodide, but no evidence of the transformation of the carbinol base into the corresponding ammonium base was obtained.

[With MATEI SASSU and WASLAW WISLOKI.]—Addition of aqueous sodium hydroxide to pyridine methiodide yields a solution, which resembles in its behaviour that obtained from an aliphatic quaternary ammonium salt, and it has therefore been assumed (Hantzsch and Kalb, Abstr., 1900, i, 113) that the base is present in solution wholly in the ammonium form. The ready oxidation of such a solution to 1-methylpyridone (Decker, Abstr., 1893, i, 279) is, however, in contradiction to this view, but is readily explicable on the assumption that there exists in aqueous solution an equilibrium between the ammonium and carbinol bases, the amount of the latter being very small in com-

parison with that of the ammonium base. On oxidation, the carbinol base is continuously removed, and the equilibrium thereby displaced until the whole of the ammonium base is converted into 1-methylpyridone.



Reasons are given in favour of the annexed formula for the compound obtained by Weil (Abstr., 1902, i, 677) by the action of alkalis on trimethylquinolide methiodide.

1-Alkylpyridones are readily prepared by oxidising 1-alkylpyridinium halides with potassium ferricyanide in aqueous sodium hydroxide in the presence of benzene. The preparation of 1-methylpyridinium salts is best accomplished by treating the extremely hygroscopic additive compound of methyl sulphate and pyridine with the acid corresponding with the salt required; the picrate, $C_{12}H_{10}O_7N_4$, is thus obtained anhydrous in needles, m. p. 113—114°, or rhombohedra, m. p. 109—110°.

1-*Propylpyridinium bromide* (*pyridine propylbromide*), prepared from pyridine and propyl bromide, yields a *cadmibromide*, $C_{16}H_{24}N_2Br_4Cd$, crystallising in white needles, m. p. 117—118°; the *chloride*, *mercurichloride*, m. p. 82°, and *platinichloride*, orange-red crystals, m. p. 19[illegible]°, are also described.

1-*Propyl-2-pyridone*, $C_8H_{11}ON$, is a light yellow liquid, b. p. 263—264°/730 mm., having a repulsive odour of fungi.

1-iso*Butylpyridinium iodide* forms very hygroscopic, light yellow crystals; the *picrate*, leaflets, m. p. 114°; the *platinichloride*, yellow leaflets, m. p. 220° (decomp.). 1-iso*Butyl-2-pyridone*, $C_9H_{13}ON$, is a yellow oil, b. p. 264—265°/725 mm.

1-iso*Amylpyridinium iodide* forms hygroscopic crystals; the *picrate*, yellow needles, m. p. 145°, and the *platinichloride*, yellow leaflets, which decompose at 200°, were also prepared. 1-iso*Amyl-2-pyridone* has b. p. 283—284°/730 mm.

3-*Bromopyridine methiodide* crystallises in hygroscopic, yellow needles, m. p. 146°, and is oxidised by potassium ferricyanide to 3-*bromo-1-methyl-2-pyridone*, which forms a brown oil, and on treatment with bromine in glacial acetic acid solution yields 3 : 5-*dibromo-1-methyl-2-pyridone*; the latter compound, which crystallises in white needles, m. p. 176°, has also been prepared (1) by the oxidation of the *additive* compound of methyl sulphate and 3 : 5-dibromopyridine; (2) by brominating 1-methylpyridone. 3 : 5-*Dibromopyridine methiodide*, obtained by the action of potassium iodide on the above-mentioned additive compound, resembles *iso*quinoline methiodide in its behaviour towards alkalis.

[With S. Pfeifer, N. Prohatzka, and A. Albertini.]—The entrance of substituents into quaternary quinoline salts considerably modifies the behaviour of the latter towards alkalis; whilst 6-aminoquinoline methiodide on treatment with aqueous sodium hydroxide undergoes no change, the dinitro- and bromonitro-derivatives are converted into the corresponding carbinol bases by dilute sodium hydrogen carbonate. It thus appears that positive substituents prevent the transformation of ammonium bases into carbinol bases, whilst

with negative substituents the transformation takes place with extraordinary ease.

6-Diacetylaminoquinoline, prepared by heating 6-aminoquinoline with acetic anhydride in benzene solution, crystallises in long, slender, white needles, m. p. 75°; the product, obtained by the interaction of the methiodide and silver chloride, yields either *6-diacetylaminoquinoline methochloride* or *6-acetylaminoquinoline methochloride*, accordingly as it is crystallised from alcohol or water.

6-Acetylamino-1-methylquinolone, prepared by oxidising *6-acetylaminoquinoline methiodide*, crystallises in needles, m. p. 278° (compare Decker and Engler, Abstr., 1903, i, 518).

6-Aminoquinoline methochloride, obtained by heating the acetyl (or diacetyl) derivative with hydrochloric acid, crystallises in citron-yellow needles, m. p. 242—243°; it separates from water in efflorescent crystals containing one molecule of the solvent; the methiodide forms reddish-brown needles, m. p. 199° (compare Claus and Schnell, Abstr., 1896, i, 319). When treated with 35% aqueous sodium hydroxide, 6-aminoquinoline methiodide yields a *substance*,

$$C_{20}H_{29}O_4N_2I,$$

crystallising in microscopic, red needles, m. p. 166°, which have a vivid green, metallic lustre, and yield solutions having a yellow fluorescence.

6 : 8-*Dinitro-2-isobutyloxy-1-methyldihydroquinoline*,

$$C_{14}H_{17}O_5N_3,$$

has m. p. 87°; the methyl and ethyl ethers (Kaufmann and Strübin, this vol., i, 322) are also described.

6-Bromo-8-nitroquinoline, which has m. p. 170—177° (compare Claus and Hartmann, Abstr., 1896, i, 391), on successive treatment with methyl sulphate and potassium iodide yields the *methiodide*, $C_{10}H_8O_2N_2BrI$, which crystallises in dark reddish-brown needles, decomposing at 185—186°. With dilute aqueous ammonia the methiodide yields *6-bromo-8-nitro-2-hydroxy-1-methyldihydroquinoline*, which has m. p. 173—175°, and forms a *methyl ether*, m. p. 121—122°; the *ethyl ether* crystallises in prisms, m. p. 111°.

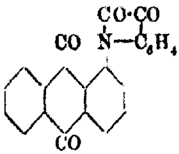
3-Bromo-8-nitro-2-hydroxy-1-methyldihydroquinoline (Decker, Abstr., 1905, i, 374) is obtained in quantitative yield by the action of very dilute aqueous ammonia on the methiodide; the *ethyl ether*, large, light brown, prismatic crystals, has m. p. 90—91°. F. B.

Preparation of Halogen-substituted Indophenol Derivatives from Carbazoles and *p*-Nitrosophenols. LEOPOLD CASSELLA & Co. (D.R.-P. 235836).—When *p*-nitrosophenol or its halogen derivatives are condensed in concentrated sulphuric acid solution with *N*-alkyl or halogenated carbazoles, indophenol derivatives of tinctorial value are produced.

The *products* from monochlorocarbazole and *p*-nitrosophenol, from carbazole and *N*-ethylcarbazole with *o*-chloronitrosophenol respectively, and from carbazole with 2 : 6-dibromonitrosophenol were prepared. They are dark blue or green substances, insoluble in water, but soluble in concentrated sulphuric acid with a blue

coloration, decompose above 250° without fusion, and yield colourless leuco-compounds. F. M. G. M.

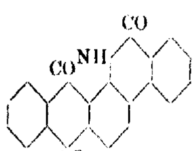
[Preparation of Anthraquinone Derivatives.] Farbenfabriken vorm. Friedr. Bayer & Co. (D.R.-P. 236407).—When α-chloroanthraquinone is boiled with isatin (in nitrobenzene solution) in the presence of cuprous chloride and copper acetate and the mixture subsequently acidified, it yields the *compound* (annexed formula) as a bluish-red, crystalline powder. The *products* from 1 : 5-dichloroanthraquinone and isatin (1 mol.), a violet powder, and the same with 2 mols. of isatin were also prepared, whilst 4-bromo-1-methylaminoanthraquinone under similar conditions yielded a greenish black powder. F. M. G. M.



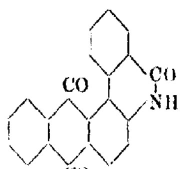
Preparation of Phenanthridone Derivatives. Badische Anilin- & Soda-Fabrik (D.R.-P. 236857).—When halogen-o-benzoylaminoanthraquinones (or their derivatives) are boiled with or without copper powder in naphthalene solution with anhydrous sodium carbonate (or acetate), condensation occurs, yielding phenanthridone derivatives.

The *compound* (I), $C_{21}H_{11}O_3N$, prepared from 2-bromo-1-benzoylaminoanthraquinone (without the addition of copper powder), crystallises from dichlorobenzene, and has m. p. 266—267°.

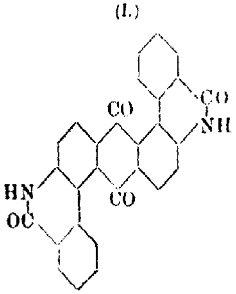
The *compound* (II), m. p. 274—275°, was obtained from 1-chloro-2-benzoylaminoanthraquinone in nitrobenzene solution without copper powder. The *products* from 2 : 3-dichloro-1 : 4-dibenzoylaminoanthra-



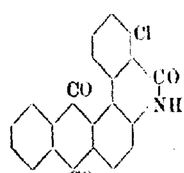
(I.)



(II.)



(III.)



(IV.)

quinone and from 3-halogen-2-benzoylaminoanthraquinone do not fuse below 325°.

The *product* (III), $C_{28}H_{14}O_4N_2$, prepared from 1 : 5-dichloro-1 : 6-dibenzoylaminoanthraquinone in the presence of copper, does not melt at 320°.

The *compound* (IV), $C_{21}H_{10}O_3NCl$, m. p. 278—280°, was obtained from 1-chloro-*o*-chlorobenzoylaminoanthraquinone (prepared from *o*-chlorobenzoyl chloride and 1-chloro-2-aminoanthraquinone).

F. M. G. M.

[Preparation of Carbamide Derivatives.] CARL JÄGER (D.R.-P. 236594).—When an aromatic *m*-diamino-sulphonic acid (1 mol.) reacts with an aminonaphtholsulphonic acid (2 mols.) and carbonyl chloride (2 mols.) in dilute aqueous sodium carbonate solution, derivatives of carbamide are obtained. The *substance*,

$$SO_3H{\cdot}C_6H_2Me[NH{\cdot}CO{\cdot}NH{\cdot}C_{10}H_5(OH){\cdot}SO_3H]_2,$$

is prepared in this manner from 2 : 6-tolylenediamine-4-sulphonic acid, 6-amino-α-naphthol-3-sulphonic acid, and carbonyl chloride. These compounds when combined with 2 mols. of a diazonium compound yield orange to bluish-red direct cotton dyes. F. M. G. M.

Catalytic Decomposition of Alkylidenehydrazines. II. NICOLAI M. KIJNER (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 951—962).—With a view to generalising the method of obtaining hydrocarbons previously described (this vol., i, 679), the author has studied the decomposition, in presence of potassium hydroxide, of the hydrazones of dihydrocarvone, carvenone, citronellaldehyde, and citral.

Under these conditions, dihydrocarvonehydrazone yields $\Delta^{8(9)}$-*p*-menthene (compare Perkin and Pickles, Trans., 1905, **87**, 639). The action of hydrobromic acid on this hydrocarbon gives the bromo-derivative, $C_{10}H_{19}Br$, which yields *i*-$\Delta^{4(8)}$-menthene (compare Wallach, Abstr., 1906, i, 682) when distilled with aniline.

Carvenonehydrazone, when distilled in presence of fused potassium hydroxide, yields Δ^3-menthene.

Citronellaldehydehydrazone yields the *hydrocarbon*,

$$CMe_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2{\cdot}CH_3,$$

b. p. 164·5°/756 mm., D_0^{20} 0·7533, n_D 1·4304, $[\alpha]_D$ + 9·28°. Oxidation of this hydrocarbon with permanganate yields acetone, active amylacetic acid (compare Welt, Abstr., 1895, i, 203), and, as an intermediate product, the *keto-alcohol*,

$$OH{\cdot}CMe_2{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CHMe{\cdot}CH_2Me,$$

b. p. 218°/755 mm., D_0^{20} 0·9069, n_D 1·4363, which reduces ammoniacal silver solution in presence of alkali, and forms a *semicarbazone*, m. p. 125—126°, $[\alpha]_D$ + 1·78° to + 2·20°.

The hydrocarbon, b. p. 164·5°, obtained from citronellaldehydehydrazone, gives with hydrobromic acid the *bromo*-derivative,

$$C_{10}H_{21}Br,$$

D_0^{20} 1·0772, n_D 1·4578, which gives a hydrocarbon, $C_{10}H_{20}$, with almost the same physical constants as the original one when distilled with aniline, with the exception of its specific rotation, which is $[\alpha]_D$ + 4·39°.

Reduction of the hydrocarbon, b. p. 164·5°, by means of hydriodic acid in a sealed tube yields βζ-dimethyloctane,

$$CHMe_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CHMeEt\ (?),$$

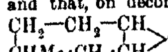
b. p. 159—159·5°/742 mm., D_4^{20} 0·7313, n_D 1·4110, $[\alpha]_D$ +1·75° (compare Markownikoff and Reformatsky, Abstr., 1893, i, 662; Skita and Ritter, *Ber.*, 1911, 44, 668; this vol., i, 272).

Citralhydrazone, when distilled with solid potassium hydroxide yields an inactive *hydrocarbon*, $CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe{:}CHMe$, b. p. 164—165°/755 mm., D_0^{20} 0·7674, n_D 1·4443, which is isomeric with the dihydromyrcene, b. p. 171·5—173·5°, obtained by Semmler (Abstr., 1901, i, 732) by the reduction of myrcene. T. H. P.

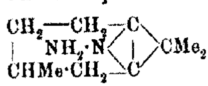
Decomposition of Alkylidenehydrazines. Conversion of Pulegone [Tanacetone] into a Bicyclic Hydrocarbon, $C_{10}H_{18}$. NICOLAI M. KIJNER and A. ZAVADOVSKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1132—1148. Compare this vol., i, 679).—The action of hydrazine hydrate on tanacetone would be expected to give an alkylidenehydrazine of the structure

$$CHMe{<}{\scriptstyle CH_2\text{———}CH_2 \atop \scriptstyle CH_2\cdot C({:}N\cdot NH_2)}{>}C{:}CMe_2,$$

this yielding, on decomposition, $\Delta^{4(8)}$-menthene (compare Wallach, Abstr., 1908, i, 402). It is found, however, that pulegohydrazine is not hydrolysed by mineral acids, with which it forms stable salts, and that, on decomposition, it gives a dicyclic hydrocarbon, *carane*,



corresponding with carone. The action of hydrazine hydrate on pulegone is hence accompanied by isomerisation, pulegohydrazine having the annexed constitution.



Pulegohydrazine, $C_{10}H_{18}N_2$, is an almost colourless liquid, b. p. 131—132°/23 mm., 143—144°/35 mm., D_0^{20} 0·9602, $[\alpha]_D$ − 5·55°, n_D 1·4943. The *thiosemicarbazone*,

$$NHPh\cdot CS\cdot NH\cdot N{:}C_{10}H_{16},$$

forms thin, rhombic plates, m. p. 176°, $[\alpha]_D$ − 114·33°. The hydrazine undergoes oxidation in the air, yielding pulegone, and an oily product which was not investigated.

Carane, $C_{10}H_{18}$, obtained by the slow distillation of pulegohydrazine with potassium hydroxide, has b. p. 169·5°/759 mm., D_0^{20} 0·8404—0·8411, n_D 1·4561—1·4576, exaltation of molecular refraction 0·72—0·85, $[\alpha]_D$ + 56·89° to 57·64°. Carane is quite saturated in character, and, owing to the presence of the trimethylene ring (indicated by the optical exaltation) readily combines with 1 mol. of bromine or halogen hydroacid. The *bromo*-derivative, $CH_2{<}{\scriptstyle CHMe\cdot CH_2 \atop \scriptstyle CH_2\text{—}CH_2}{>}CH\cdot CMe_2Br$, obtained by the action of hydrobromic acid, has b. p. 123—124°/29 mm (slightly decomp.), D_4^{20} 1·1811, D_0^{20} 1·1691, n_D 1·4893—1·4914, $[\alpha]_D$ + 5·37° to 5·42°, and loses hydrogen bromide in two different ways: (1) with alcoholic potassium hydroxide it gives $\Delta^{3(8)}$-*m*-menthene (compare Wallach, *loc. cit.*), which yields β-methyladipic acid when oxidised with excess of permanganate; (2) with aniline the principal

product is $\Delta^{4(8)}$-*m-menthene*, $CH_2<\substack{CHMe\cdot CH_2 \\ CH_2-CH_2}>CH\cdot CMe\colon CH_2$, which is, however, mixed with $\Delta^{8(9)}$-*m*-menthene.

When $\Delta^{8(9)}$-*m*-menthene is treated with hydriodic acid and the iodide heated with aqueous-alcoholic potassium hydroxide, $\Delta^{4(8)}$-*m*-menthene is obtained.

Reduction of carane or $\Delta^{8(9)}$-*m*-menthene yields *m*-menthane.

Combination of carane with bromine (1 mol.) and distillation of the bromide thus obtained with quinoline gives lævorotatory menthadiene, which, after prolonged boiling with sodium, becomes inactive, and has b. p. 182—185°/749 mm., D_4^{20} 0·8544, n_D 1·4916; this hydrocarbon in acetic anhydride solution gives an intense blue coloration with sulphuric acid. Such a coloration is given by $\Delta^{2:8(9)}$-*m*-menthadiene (compare Haworth, Perkin, and Wallach, Trans., 1911, **99**, 118), but this could only be derived from carane as a result of isomerisation of the bromide previous to the removal of hydrogen bromide (see also Perkin, Trans., 1910, **97**, 2154). T. H. P.

Influence of Auxochromes on Phototropy. MAURICE PADOA and L. SANTI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 196—200. Compare this vol., i, 693).—On comparing the phototropic substances previously obtained, it appears that the aldehydrazones which contain auxochrome groups are generally more phototropic than those which do not contain any, and this is even more noticeable in the case of the osazones of diketones. The position of the auxochrome appears to have some influence. In the present paper eight anishydrazones (*p*-methoxyphenylhydrazones) are described, which have been prepared for comparison with the corresponding phenylhydrazones.

p-Methoxyphenylhydrazine (compare Altschul, Abstr., 1892, 1080) is best obtained by diazotising *p*-anisidine and reducing the diazonium compounds with stannous chloride. It has m. p. 66° (Altschul, 65°).

Benzaldehyde-p-*methoxyphenylhydrazone*, $OMe\cdot C_6H_4\cdot NH\cdot N\colon CHPh$, crystallises in pale yellow needles, m. p. 123°, and is phototropic.

Anisaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot OMe,$$

forms lustrous, yellow scales, m. p. 126°, and is not phototropic.

Cinnamaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot CH\colon CHPh,$$

crystallises in rosettes of short, thick needles, m. p. 126·5°, and is phototropic.

Cuminaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4\cdot CHMe_2,$$

forms long, pale yellow needles, m. p. 99°. It is phototropic.

Piperonaldehyde-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_3\colon O_2\colon CH_2,$$

crystallises in yellowish-green, lustrous needles, m. p. 134—135°, and is phototropic.

p-*Tolualdehyde*-p-*methoxyphenylhydrazone*,

$$OMe\cdot C_6H_4\cdot NH\cdot N\colon CH\cdot C_6H_4Me,$$

forms lustrous, yellow scales, m. p. 131°, and is not phototropic.

Vanillin-p-methoxyphenylhydrazone,

$$OMe\cdot C_6H_4\cdot NH\cdot N:CH\cdot C_6H_3(OH)\cdot OMe,$$

crystallises in minute, pale yellow prisms, m. p. 125—126°, and is phototropic.

Salicylaldehyde-p-methoxyphenylhydrazone,

$$OMe\cdot C_6H_4\cdot NH\cdot N:CH\cdot C_6H_4\cdot OH,$$

forms yellowish-green needles, m. p. 137°, and is not phototropic.

R. V. S.

Phototropy of the Hydrazones of Furfuraldehyde. L. Santi (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 228—230. Compare Padoa and Graziani, Abstr., 1910, i, 509, 778).—Furfuraldehyde-phenylhydrazone is not phototropic.

Furfuraldehyde-a-naphthylhydrazone, $C_4H_3O\cdot CH:N\cdot NH\cdot C_{10}H_7$, forms small, canary-yellow prisms, m. p. 110·5°, and is not phototropic.

Furfuraldehyde-β-naphthylhydrazone crystallises in pale yellow needles, m. p. 137°, and is phototropic.

Furfuraldehyde-p-tolylhydrazone, $C_4H_3O\cdot CH:N\cdot NH\cdot C_6H_4Me$, is a pale yellow, crystalline powder, which is weakly phototropic.

R. V. S.

Action of Aldehydes on Pyrrole Derivatives. U. Colacicchi (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 312—317).—Pyrrole derivatives which have only one free methine hydrogen, and have a negative substituent, react with aliphatic aldehydes when warmed with them in the presence of a little zinc chloride. The condensations with formaldehyde are best effected in the presence of hydrochloric acid.

Bis-5-acetyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Ac)_2$, forms yellow scales or needles, m. p. 272°.

Bis-3-acetyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Ac)_2$, is a yellow, crystalline powder, m. p. 268°.

Bis-5-benzoyl-2 : 4-dimethylpyrrylmethane, $CH_2(C_4NHMe_2Bz)_2$, crystallises in small, colourless needles, m. p. 257—258°.

aa-Bis-5-acetyl-2 : 4-dimethylpyrrylethane $CHMe(C_4NHMe_2Ac)_2$, forms yellow needles, m. p. 253°.

aa-Bis-3-acetyl-2 : 4-dimethylpyrrylethane, $CHMe(C_4NHMe_2Ac)_2$, crystallises in pale, rose-coloured scales, m. p. 254°.

aa-Bis-5-benzoyl-2 : 4-dimethylpyrrylethane, $CHMe(C_4NHMe_2Bz)_2$, forms very small prisms, m. p. 244—245°.

aa-Bis-5-benzoyl-2 : 4-dimethylpyrrylbutane, $CHPr(C_4NHMe_2Bz)_2$, crystallises in small, yellow prisms, m. p. 217—218°.

aa-Bis-5-benzoyl-2 : 4-dimethylpyrrylisobutane,

$$CHMe_2\cdot CH(C_4NHMe_2Bz)_2,$$

is a yellow, flocculent substance, which on heating becomes soft at 80°, spongy at 100°, and melts at 180°.

aa-Bis-5-benzoyl-2 : 4-dimethylpyrrylheptane,

$$C_6H_{13}\cdot CH(C_4NHMe_2Bz)_2,$$

forms a yellow, crystalline powder, m. p. 178—179°. R. V. S.

Preparation of Halogenated Derivatives of Indigotin. Badische Anilin- & Soda-Fabrik (D.R.-P. 235631. Compare this vol., i, 925).—The preparation of tetrahalogenated indigotins has

previously been recorded; penta- and hexa-halogenated derivatives have now been prepared.

Dichlorotetrabromoindigotin is obtained when 4 : 4'-dichloroindigotin, dissolved in nitrobenzene (or acetic acid), is slowly treated with bromine and the mixture subsequently boiled until the evolution of hydrogen bromide ceases.

Pentachloroindigotin is prepared by the further chlorination of 4 : 4'-dichloroindigotin at 25—30° in acetic acid solution. The leuco-derivatives and intermediate halogenated acetylindigotins are also mentioned and their tinctorial properties described. F. M. G. M.

Hydantoins. VI. Action of Acylthioncarbamates, Acylthiocarbamates, Acyldithiocarbamates, and Acylimidodithiocarbonates on α-Amino-acids. 2-Thiolhydantoin. HENRY L. WHEELER, BEN H. NICOLET, and TREAT B. JOHNSON (*Amer. Chem. J.*, 1911, 46, 456—474).—This work was undertaken for the purpose of synthesising some *N*-acyl derivatives of hydantoic and thiohydantoic acids and of investigating their behaviour on hydrolysis and their reactivity towards aldehydes.

Benzoyl-ψ-ethylhydantoic acid, $NBz\colon C(OEt)\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 161°, obtained by the action of aminoacetic acid on ethyl benzoylthioncarbamate in presence of potassium hydroxide, crystallises in needles; its *ethyl* ester has m. p. 79—80°. *Ethyl benzoyl-ψ-methylhydantoate*, $NBz\colon C(OMe)\cdot NH\cdot CH_2\cdot CO_2Et$, m. p. 103°, is obtained by the interaction of ethyl aminoacetate and methyl benzoylthioncarbamate. When benzoyl-ψ-ethylhydantoic acid or ethyl benzoyl-ψ-methylhydantoate is hydrolysed with hydrochloric acid, *benzoylhydantoic acid*, $NHBz\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 253—254° (decomp.), is produced, which crystallises in plates, and is decomposed by hydrochloric acid into benzoic acid and hydantoin. An attempt to condense benzoylhydantoic acid with benzaldehyde was not successful.

Thiobenzoylhydantoic acid, $NHBz\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. 202°, prepared by heating a mixture of aminoacetic acid, potassium hydroxide, and ethyl benzoyldithiocarbamate, crystallises in plates or needles; its *ethyl* ester has m. p. 128—129°. When either thiobenzoylhydantoic acid or thioacetylhydantoic acid is heated with concentrated hydrochloric acid, 2-*thiohydantoin*, $CH_2<\begin{matrix}CO-NH\\ NH\cdot CS\end{matrix}$, m. p. 227°, is produced, which forms yellow prisms. Benzoylthiohydantoic acid condenses with benzaldehyde to form 2-*thio*-1-*benzoyl*-4-*benzylidenehydantoin*, $CHPh\colon C<\begin{matrix}CO-NBz\\ NH\cdot CS\end{matrix}$, m. p. 181°, which crystallises in rectangular plates, and is decomposed by potassium hydroxide solution with production of 2-thio-4-benzylidenehydantoin, m. p. 258°, which can also be obtained by the condensation of thiohydantoin with benzaldehyde. Ruhemann and Stapleton (Trans., 1900, 77, 246) have stated that this compound has m. p. 280° (decomp.) when heated slowly and m. p. 300° (decomp.) when heated rapidly, but the authors found the m. p. 258° under all conditions.

Thiobenzoyl-ψ-ethylhydantoic acid, $NBz\colon C(SEt)\cdot NH\cdot CH_2\cdot CO_2H$, m. p.

198°, prepared from aminoacetic acid and ethyl benzoyliminodithiocarbonate, forms clusters of needles; its *ethyl* ester has m. p. 77—78°.

Thioacetylhydantoic acid, $NHAc\cdot CS\cdot NH\cdot CH_2\cdot CO_2H$, m. p. [illegible] (decomp.), from aminoacetic acid and ethyl acetyldithiocarbamate, crystallises in slender needles; its *potassium* salt has m. p. 225—[illegible] (decomp.), and its *ethyl* ester, m. p. 104—105°. The acid condenses with benzaldehyde to form 2-*thio-1-acetyl-4-benzylidenehydantoin*, $CHPh:C<\begin{matrix}CO-NAc\\ NH\cdot CS\end{matrix}$, m. p. 231°, which crystallises in light yellow prisms.

Thio-1-acetyl-4-methylhydantoic acid, $NHAc\cdot CS\cdot NH\cdot CHMe\cdot CO_2H$, m. p. 171°, from alanine and ethyl acetyldithiocarbamate, crystallises in prisms, and is converted by concentrated hydrochloric acid into 2-*thio-4-methylhydantoin*, $CHMe<\begin{matrix}CO-NH\\ NH\cdot CS\end{matrix}$, m. p. 158—159°, which forms flat prisms.

E. G.

Preparation of 5:5-Dialkylthiobarbituric Acids. EMANUEL MERCK (D.R.-P. 235801. Compare this vol., i, 683).—The preparation of 5:5-dialkylthiobarbituric acids by the employment of metallic alkyloxides has previously been described; it is found that these can be replaced by the free alkali metal (or its amide), and the preparation of diethylthiobarbituric acid (m. p. 180°) from diethylmalonic ester, thiocarbamide, and sodamide (or metallic sodium) is now demonstrated.

F. M. G. M.

Constitution of the Nitro-2:5-dimethylbenziminazole Obtained by Nitration. DAVID MARON and D. SALZBERG (*Ber.*, 1911, **44**, 2999—3005).—The proof that the nitro-group in the nitro-compound, m. p. 200—201°, obtained by the nitration of 2:5-dimethylbenziminazole (Niementowsky, Abstr., 1886, 719), occupies position 6 is as follows. By reduction with iron and 50% acetic acid, the nitro-compound yields an *amine*, m. p. 85°, the *acetyl* derivative of which has m. p. 263—264°. By nitration, diacetyl-*m*-tolylenediamine yields a nitro-compound, which can be reduced to an *amine*, m. p. 252—253°, which forms an azoimide with nitrous acid (therefore the amino-group is ortho to an NHAc group), and yields the preceding acetylaminodimethylbenziminazole, m. p. 263—264°, by heating at 250°. Finally, the nitration of diacetyl-3:4-tolylenediamine yields a nitro-compound, the reduction of which yields an *amine*, m. p. 238°, the *acetyl* derivative of which, m. p. 273—274°, is identical with that obtained by the acetylation of the preceding amine, m. p. 252—253°. Consequently, this acetylated triamino-derivative must be triacetyl-3:4:6-triaminotoluene; the amine m. p. 238° is 6-aminodiacetyl-3:4-tolylenediamine, the amine m. p. 252—253° is 3-aminodiacetyl-4:6-tolylenediamine, and the nitrated dimethylbenziminazole is 6-nitro-2:5-dimethylbenziminazole.

C. S.

Researches on Azinetriphenylpyrrole. FRANCESCO ANGELICO (*Gazzetta*, 1911, **41**, ii, 378—381).—By the action of ammonium sulphide on the diketone, $\begin{matrix}CH:CH\cdot C-N:N\\ CH:CH\cdot C\cdot CBz:CBz\end{matrix}$ (compare Abstr., 1909,

i, 127), the author obtained (Abstr., 1910, i, 444) the corresponding dithioketone, m. p. 206°, and he has now isolated from the product of the same reaction, a thiophen *compound*, $C_{22}H_{14}N_2S$, which forms large, yellow needles, m. p. 151°. When treated with nitric acid this substance regenerates the ketone of m. p. 163°.

The structure of the dithioketone follows from the fact that both it and the diketone yield, when treated with hydroxylamine, the same products, namely: (1) a red pyrrole derivative; (2) a substance, probably a mixture of mono- and di-oximes; (3) a *substance*, $C_{44}H_{27}O_4N_9$, which crystallises in golden-yellow needles, m. p. 205—206°.

R. V. S.

5-Aminophenazoxonium Salts. FRIEDRICH KEHRMANN and L. LOWRY (*Ber.*, 1911, 44, 3006—3011).—5-Aminophenazoxonium and 5-aminophenazthionium salts cannot be prepared in a similar manner to 5-aminophenylphenazonium salts (Kehrmann and Masslenikoff, this vol., i, 927). However, by the reduction of Ullmann and Kuhn's 5-nitrophenoxazine (Abstr., 1909, i, 173) by stannous chloride and concentrated hydrochloric acid, 5-*aminophenoxazine hydrochloride*, $C_6H_4{<}{}^{NH}_{O}{>}C_6H_3\cdot NH_2,HCl$, is obtained, which is oxidised by cold concentrated ferric chloride to 5-*aminophenazoxonium chloride*, $C_6H_4{<}{}^{N}_{OCl}{>}C_6H_3\cdot NH_2$, greenish-black crystals; the corresponding *bromide*, *iodide*, *nitrate*, and *platinichloride* are described.

When acetylated by sodium acetate, acetic anhydride, and a trace of zinc dust, 5-aminophenoxazine hydrochloride yields 5-*acetylaminophenoxazine*, m. p. 197° (decomp.), colourless needles, which is oxidised by ferric chloride to a mixture of two substances, m. p. about 215° (decomp.), which are probably isomeric 5-acetylaminophenazoxones.

3:5-Diaminophenazoxonium chloride reacts with acetic anhydride and zinc chloride to form a blackish-red, crystalline *zincichloride*, from which 3-*amino*-5-*acetylaminophenazoxonium chloride*,

$$C_6H_4{<}{}^{N}_{OCl}{>}C_6H_2(NH_2)\cdot NHAc,H_2O,$$

is obtained in dark red prisms with a green lustre. The *platinichloride* is a brownish-red, crystalline powder, whilst the *base* itself, m. p. 185—190° (decomp.), crystallises in citron-yellow needles.

C. S.

Mutual Replacement of Azines and Semicarbazones. GUSTAV KNÖPFER (*Monatsh.*, 1911, 32, 753—772).—It has been shown previously that the azine residue is readily replaced by phenylhydrazine, and this in turn by semicarbazide (Knöpfer, Abstr., 1909, i, 188; 1910, i, 432). It is now found that azines are very easily converted into semicarbazones, but that in most instances the reverse change does not take place. When aldehydes or ketones are treated with a molecular mixture of semicarbazide and hydrazine, the semicarbazone is, as a rule, the sole product.

The conversion into azine was observed in the case of the semicarbazones of salicylaldehyde, *p*-hydroxybenzaldehyde, *p*-nitrobenz

aldehyde, resorcylaldehyde, protocatechualdehyde, *p*-dimethylaminobenzaldehyde, and acetone.

The *azine* of phenyl ethyl ketone forms yellow needles, m. p. 79—80°. The semicarbazone forms colourless crystals, m. p. 179—180°.

Distyryl ketone-semicarbazone forms colourless, soluble needles, m. p. 187—190°; *a-dichloroacetonesemicarbazone* has m. p. 163°, yielding a compound, m. p. 254°, which proved to be methylglyoxaldisemicarbazone.

Chloralhydrazide, $CCl_3 \cdot CH(OH) \cdot NH \cdot NH_2$, forms large, colourless crystals, m. p. 85° (decomp.). The hydrazide is readily replaced by semicarbazide, forming chloral semicarbazide, m. p. 90°, but the reverse change does not take place.

The only substances to give both semicarbazone and azine on treatment with an equimolecular mixture of the two bases are *p*-nitrobenzaldehyde and *p*-dimethylaminobenzaldehyde. E. F. A.

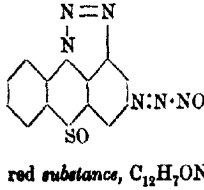
3 : 5 - Diaminophenazthionium Derivatives. FRIEDRICH KEHRMANN and J. STEINBERG (*Ber.*, 1911, **44**, 3011—3017).—The course of the reaction between picryl chloride and *o*-aminophenyl mercaptan proceeds, as stated by Kehrmann and Schild (Abstr., 1900, i, 61), not as by Mitsugi, Beyschlag, and Möhlau (Abstr., 1910, i, 337), the proof being as follows. A hot alcoholic solution of picryl chloride (2 mols.) condenses normally with *oo'*-diaminodiphenyl disulphide hydrochloride in the presence of sodium acetate, yielding *oo'-dipicryl diaminodiphenyl disulphide*, $[C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4]_2S_2$, which is reduced by alcoholic sodium sulphide to *o-picrylaminophenyl mercaptan*, $C_6H_2(NO_2)_3 \cdot NH \cdot C_6H_4 \cdot SH$. The latter, in which the picryl group must be attached to the nitrogen atom, is converted by warm aqueous sodium hydroxide into the same dinitrophenthiazine as results from the condensation of *o*-aminophenyl mercaptan and picryl chloride; consequently in this condensation the amino-, not the sulphydryl, group reacts with the chlorine atom of the picryl chloride.

3 : 5-Diaminophenazthionium chloride, acetic anhydride, and zinc chloride react to form a violet-black, crystalline *zincichloride*, from which *3-amino-5-acetylaminophenazthionium chloride*,

$$C_6H_4 {<}^{N}_{SCl}{>} C_6H_2(NH_2) \cdot NHAc,$$

can be obtained in violet needles; the corresponding *nitrate*, *platinichloride*, and *dichromate* are described, whilst the *base* itself, $C_{14}H_{11}ON_3S$, crystallises in brick-red needles.

In the hope of eliminating an amino-group, 3 : 5-diaminophenazthionium chloride, dissolved in moderately-concentrated sulphuric acid, has been treated with 10% sodium nitrite at 0°; however, the product, isolated as the *nitrate*, brownish-yellow needles, appears to be a diazonium salt of the annexed constitution from its analysis, explosiveness, and general behaviour. When treated with boiling water containing a little sulphuric acid, nitrogen is evolved, and a brownish-red *substance*, $C_{12}H_7ON_3S$, is obtained. C. S.



Preparation of 5:5-Dialkyliminobarbituric Acids (2-Imino-4:6-diketo-5-dialkylpyrimidines). EMANUEL MERCK (D.R.-P. 235803).—**Dialkylmalonic esters react with guanidine in the presence of condensing agents to yield dialkylmalonylguanidines (5:5-dialkyliminobarbituric acids).**

2-Imino-5:5-diethylbarbituric acid, $CEt_2<\genfrac{}{}{0pt}{}{CO\cdot NH}{CO\cdot NH}>C{:}NH$, colourless needles, which on heating decompose without fusion, forms a crystalline *nitrate*, and on boiling with mineral acids furnishes diethylbarbituric acid, m. p. 191°. F. M. G. M.

1-Phenyl-5-methyl-1:2:4-triazole and Cyanophenylacetamidine. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, ii, 93—100. Compare following abstract).—Bladin (Abstr., 1891, 472) described 1-phenyl-5-methyl-1:2:4-triazole (at first erroneously as 1-phenyl-3-methyl-1:2:4-triazole) as an uncrystallisable oil, b. p. about 250°, whilst Bamberger and Gruyter (Abstr., 1894, i, 23) recorded the same substance as a crystalline solid, m. p. 191°. The author has prepared 1-phenyl-5-methyl-1:2:4-triazole from formylphenylhydrazine and acetamide (compare following abstract), and finds that it is identical with the substance described by Bladin. The substance, m. p. 191°, of Bamberger and Gruyter is cyanophenylacetamidine,

$$NPh{:}CMe\cdot NH\cdot CN,$$

identical with that obtained from ethyl*iso*acetanilide and cyanamide by the method used by Comstock and Wheeler (Abstr., 1892, 747) for cyanophenylformamidine. Cyanophenylacetamidine has m. p. 193°. With warm potassium hydroxide it yields acetanilide and cyanamide. When treated with concentrated hydrochloric acid, it takes up water with formation of carbamidophenylacetamidine, $NPh{:}CMe\cdot NH\cdot CO\cdot NH_2$, which crystallises in lustrous plates, m. p. 180° (decomp.) if rapidly heated, or about 166° if slowly heated.

R. V. S.

Triazole and its Derivatives. GUIDO PELLIZZARI (*Gazzetta*, 1911, **41**, ii, 20—42. Compare Abstr., 1895, i, 308; Pellizzari and Massa, Abstr., 1897, i, 205; 1901, i, 488).—The author gives a summary of the triazole derivatives which have been prepared by himself and his collaborators, and describes a number of other compounds obtained in the same way. Some of these have been prepared already by other investigators by different methods.

2-Phenyl-1:3:4-triazole (compare Young, Trans., 1901, **79**, 659) can be prepared from benzoylhydrazine and formamide, or from formylhydrazine and benzamide. The *hydrochloride*, $C_8H_7N_3,HCl$, forms colourless needles, m. p. 195°. The *platinichloride*,

$$(C_8H_7N_3)_2,H_2PtCl_6,2H_2O,$$

crystallises in orange-yellow plates, decomposing at 255°. Young obtained this salt with $3H_2O$. The platinic chloride compound, $(C_8H_7N_3)_2PtCl_4$, obtained by boiling the preceding salt with water, is a yellow, flocculent substance.

2:5-Dimethyl-1:3:4-triazole (compare Stollé, Abstr., 1904, i, 453) can be prepared from acetylhydrazine and acetamide.

2 : 5-Diphenyl-1 : 3 : 4-triazole (compare Pinner, Abstr., 1894, i, [illegible]) can be obtained from benzoylhydrazine and benzanilide.

1-Phenyl-3-methyl-1 : 2 : 4-triazole (compare Andreocci, Abstr., 1892, **i, 636) is obtained, mixed with 1-phenyl-1 : 2 : 4-triazole** and 1-phenyl-**5-methyl-1 : 2 : 4-triazole, by the action of acetylphenylhy**drazine on **formamide. The 1-phenyl-1 : 2 : 4-triazole is separated** with the aid of **the insolubility of its** *nitrate*, $C_8H_7N_3,HNO_3$, **which** forms white **needles, m. p. 141°. 1-*Phenyl*-1 : 2 : 4-*triazole picrate*,** $C_8H_7N_3,C_6H_3O_7N_3$, **has m. p. 159°. 1-*Phenyl-3-methyl*-1 : 2 : 4-*triazole picrate*,**

$$C_9H_9N_3,C_6H_3O_7N_3,$$

forms long, pale yellow needles, m. p. 171°.

1-Phenyl-5-methyl-1 : 2 : 4-triazole, b. p. 275° (compare preceding abstract), can be obtained from formylphenylhydrazine and acetamide. It is mixed with 1-phenyl-1 : 2 : 4-triazole and 1-phenyl-3-methyl-1 : 2 : 4-triazole, of which the former can be removed in the form of nitrate, and the latter by distillation. 1-*Phenyl-5-methyl*-1 : 2 : 4-*triazole picrate*, $C_9H_9N_3,C_6H_3O_7N_3$, forms short, prismatic crystals, m. p. 146°. The *platinichloride*, $(C_9H_9N_3)_2,H_2PtCl_6,2H_2O$, crystallises in yellow plates, m. p. 129° (decomp.). The *platinic chloride* compound, $(C_9H_9N_3)_2,PtCl_4$, is obtained as a pale yellow precipitate by boiling the preceding substance with water. 1-Phenyl-5-methyl-1 : 2 : 4-triazole yields the same methyltriazole as 1-phenyl-3-methyl-1 : 2 : 4-triazole (compare Andreocci, *loc. cit.*), so that there is only one 3-methyl-1 : 2 : 4-triazole.

1 : 3 : 5-Triphenyl-1 : 2 : 4-triazole (compare Engelhard, Abstr., 1897, i, 127) can be obtained: (1) from benzamide and β-benzoylphenylhydrazine; (2) from benzamide and α-benzoylphenylhydrazine; (3) from dibenzoylphenylhydrazine and ammonia. Its *hydrochloride* crystallises in needles, m. p. 174°.

1-*Phenyl*-3 : 5-*dimethyl*-1 : 2 : 4-*triazole*, $C_{10}H_{11}N_3$, from acetamide and acetylphenylhydrazine, forms colourless crystals, m. p. 43°, b. p. 281°. The *platinichloride*, $(C_{10}H_{11}N_3)_2,H_2PtCl_6,2H_2O$, forms orange-coloured, acicular crystals, m. p. 185—186°; the anhydrous salt has m. p. 195°. The *picrate*, $C_{10}H_{11}N_3,C_6H_3O_7N_3$, crystallises in long, yellow needles, m. p. 156°.

1-*Phenyl-2-methyl*-1 : 3 : 4-*triazole*, $C_9H_9N_3$, from acetylphenylhydrazine and formanilide, forms laminar crystals (containing $1H_2O$), m. p. 68°; the anhydrous salt has m. p. 112°. The *picrate*, $C_9H_9N_3,C_6H_3O_7N_3$, has m. p. 134°. The *platinichloride*, $(C_9H_9N_3)_2,H_2PtCl_6$, crystallises in orange-coloured laminæ, m. p. 206°; when it is boiled with water the *platinic chloride* compound, $(C_9H_9N_3)_2,PtCl_4$, is obtained as a pale yellow precipitate. R. V. S.

Action of Acetyl Chloride on Acetylbiuret. Adriano Ostrogovich (*Gazzetta*, 1911, **41**, ii, 70—74).—Further examination of the base obtained by the action of acetyl chloride on acetylbiuret (compare Abstr., 1898, i, 336) has shown that it is diketomethyltriazine (identical with that of Nencki, *Ber.*, 1876, **9**, 234), formed by a dehydration analogous to that which occurs in the case of acetylguanylcarbamide (compare Abstr., 1909, i, 461):

$$COMe{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}CO{\cdot}NH_2 = H_2O + NH{<}{\substack{CMe{=}N\\CO{\cdot}NH}}{>}CO.$$

This method is the most convenient for the synthesis of the substance, since it is only necessary to heat biuret with an excess of acetyl chloride for two or three hours at 100°, and then to raise the temperature to 140—145° for about four hours. R. V. S.

5-Aminopyrazoles and Iminopyrines. II. AUGUST MICHAELIS (*Annalen*, 1911, **385**, 1—43. Compare Abstr., 1905, i, 476).—The paper contains a description of the derivatives of 5-anilo- and 5-tolyliminopyrazolones (5-anilino- and 5-toluidino-pyrazoles). A general method of preparing these substances is the heating of the primary aromatic base and antipyrine chloride or the 2-methochlorides of other 5-chloropyrazoles at 200°.

5-Anilo-1-phenyl-3-methylpyrazolone (*5-anilino-1-phenyl-3-methylpyrazole*), $NPh{:}C{<}\begin{matrix}NPh\cdot N\\ CH_2\cdot CMe\end{matrix}$ or $NHPh\cdot C{<}\begin{matrix}NPh{:}N\\ CH{-}CMe\end{matrix}$, m. p. 120°, b. p. 365—366°, thus prepared from aniline and antipyrine chloride forms a *hydrochloride*, $C_{16}H_{15}N_3,HCl$, m. p. 118°, *platinichloride*, m. p. 135°, *hydriodide*, $C_{16}H_{15}N_3,HI,H_2O$, m. p. 110°, *nitrate*, m. p. 150°, and *hydrogen sulphate*, m. p. 153°. [With FELIX RISSE.]—It is converted by concentrated hydrochloric acid and sodium nitrite in a freezing mixture into *4-oximino-5-anilo-1-phenyl-3-methylpyrazolone* (*4-nitroso-5-anilino-1-phenyl-3-methylpyrazole*), m. p. 168°, deep green needles (*hydrochloride*, $C_{16}H_{14}ON_4,HCl$, yellow needles). This nitroso-compound is unstable in solution, readily changing to the isomeric *3 : 4-diphenyl-6-methyldihydropyrazofurazan*, $N{<}\begin{matrix}NPh\cdot C\cdot NPh\\ CMe\cdot C{-}NH\end{matrix}{>}O$, m. p. 157°, yellow needles, which is also obtained by the action of concentrated hydrochloric acid and sodium nitrite (in small excess) on 5-anilino-1-phenyl-3-methylpyrazole at a moderate temperature.

4-Amino-5-anilino-1-phenyl-3-methylpyrazole, $C_{16}H_{16}N_4$, m. p. 140—141°, white needles, obtained by the reduction of the nitroso-compound, forms a *hydrochloride*, m. p. 240°, *phenylcarbamide*, m. p. 220°, *phenylthiocarbamide*, m. p. 160°, and *acetyl* derivative, m. p. 130 (decomp.), and is converted by sodium nitrite and warm dilute acetic acid into *3 : 4-diphenyl-6-methylaziminopyrazole*,

$$N{<}\begin{matrix}NPh\cdot C\cdot NPh\\ CMe\cdot C{-\!-}N\end{matrix}{>}N,$$

white needles, m. p. 152°.

5-p-Nitroanilino-1-phenyl-3-methylpyrazolone,

$$NO_2\cdot C_6H_4\cdot N{:}C{<}\begin{matrix}NPh\cdot N\\ CH_2{-}CMe\end{matrix},$$

yellow needles, m. p. 153°, can be obtained in bad yield by the action of concentrated nitric acid on the anilophenylmethylpyrazolone, but is best prepared by heating 2 : 5-*p*-nitroanilopyrine hydrochloride or hydriodide (following abstract); the m-*nitro*-isomeride, m. p. 138°, has been obtained by a method similar to the latter.

[With FRITZ ISERT.]—*5-Anilo-1-p-bromophenyl-3-methylpyrazolone*, $C_{16}H_{14}N_3Br$, m. p. 106°, is obtained by distilling *p*-bromoanilopyrine (2 : 5-*endo*anilo-1-*p*-bromophenyl-2 : 3-dimethylpyrazole) hydro-

chloride (following abstract) under 11 mm. pressure, or by heating aniline and 5-chloro-1-*p*-bromophenyl-3-methylpyrazole-2-methochloride at 200°; the corresponding p-*chloro*-compound has m. p. 94°.

[With W. Thomas.]—5-p-*Bromoanilo*-1-*phenyl*-3-*methylpyrazolone*, m. p. 136°, and the corresponding *chloro*-compound, m. p. 139°, are obtained by methods similar to the preceding. The action of bromine (3 mols.) in acetic acid on 5-anilo-1-phenyl-3-methylpyrazolone produces a tribrominated *substance*, m. p. 131° (4-*bromo*-5-*bromoanilo*-1-*bromophenyl*-3-*methylpyrazolone*?), which certainly contains a bromine atom in position 4, since it is unattacked by nitrous acid.

[With Felix Risse.]—5-*Anilo*-1-*phenyl*-4-*benzylidene*-3-*methylpyrazolone*, m. p. 164°, yellow prisms, and the corresponding *anisylidene* derivative, m. p. 205°, yellow needles, are prepared by heating the anilophenylmethylpyrazolone and benzaldehyde or anisaldehyde with zinc chloride at 125° for four to five hours.

[With Felix Abraham.]—The reduction of 4-nitroso-5-methylanilino-1-phenyl-3-methylpyrazole (4-nitroso-ψ-anilopyrine) (Abstr., 1908, i, 61) yields 4-*amino*-5-*methylanilino*-1-*phenyl*-3-*methylpyrazole*,

$$NMePh\cdot C{<}\begin{matrix}NPh—N\\ C(NH_2)\cdot CMe\end{matrix}$$

m. p. 85°, which forms a *hydrochloride*, m. p. 197°, *benzylidene* derivative, m. p. 101° (by means of which the base is best purified), *salicylidene* derivative, m. p. 133°, *cinnamylidene* derivative, m. p. 114°, *benzoyl* derivative, m. p. 167°, and *carbamide*, $C_{17}H_{18}N_3\cdot NH\cdot CO\cdot NH_2$, m. p. 193°. By diazotisation, 4-amino-ψ-anilopyrine yields a stable, crystalline *diazo-ψ-anilopyrine chloride*, which couples with β-naphthol to form a red, crystalline *substance*, $C_{17}H_{18}N_3\cdot N_2\cdot C_{10}H_6\cdot OH$, m. p. 173°. 4-*Amino*-5-*ethylanilino*-1-*phenyl*-3-*methylpyrazole* (4-*amino*-ψ-*ethylanilopyrine*), obtained by the reduction of 4-nitroso-ψ-ethylanilopyrine (Abstr., 1908, i, 61), crystallises in white leaflets, has m. p. 129·5°, and forms a *hydrochloride*, $C_{18}H_{20}N_4,HCl$, m. p. 220°, and *benzoyl* derivative, m. p. 208°. 5-Anilino-1-phenyl-3-methylpyrazole cannot be acetylated (or alkylated) directly, but 5-*acetylanilino*-1-*phenyl*-3-*methylpyrazole*, $NPhAc\cdot C{<}\begin{matrix}NPh\cdot N\\ CH—CMe\end{matrix}$, m. p. 96°, can be prepared by distilling a solution of anilopyrine in chloroform with acetyl chloride, at first under ordinary, and finally under reduced, pressure.

5-p-*Nitromethylanilino*-1-*phenyl*-3-*methylpyrazole*,

$$NO_2\cdot C_6H_4\cdot NMe\cdot C{<}\begin{matrix}NPh\cdot N\\ CH—CMe\end{matrix}$$

m. p. 174°, and the meta-*isomeride*, m. p. 125°, form stout, yellow crystals, and are prepared by heating the methiodides of the corresponding 2 : 5-nitroanilopyrines. 5-p-*Chloromethylanilino*-1-*phenyl*-3-*methylpyrazole* and the corresponding *p*-bromo-*compound* have m. p. 61° and 84° respectively, whilst the isomeric 5-*anilino*-1-p-*chlorophenyl*-2 : 3-*dimethylpyrazole* and 5-*anilino*-1-p-*bromophenyl*-2 : 3-*dimethylpyrazole* have m. p. 126° and 120° respectively.

[With Friedrich Walter.]—5-*Anilo*-1-*phenylpyrazolone*,

$$NPh{:}C{<}\begin{matrix}NPh\cdot N\\ CH_2—CH\end{matrix}$$

m. p. 138°, is prepared by heating 5-chloro-1-phenylpyrazole-2-meth-

iodide (following abstract) with aniline (2 mols.) at 200°, forms a green, crystalline 4-oximino-(or *nitroso*-)-compound, m. p. 113°, and yields a *methiodide* (identical with 2 : 5-anilo-1-phenyl-2-methylpyrazole hydriodide [following abstract]) with methyl iodide at 110—120°, an *ethiodide*, m. p. 149°, and a *propiodide*, m. p. 165°. 5-*Methylanilino*-1-*phenylpyrazole*, m. p. 51°, prepared by heating 5-anilo-1-phenyl-2-methylpyrazole methiodide under 13 mm. pressure, forms a stable, dark green 4-*nitroso*-derivative, m. p. 99°.

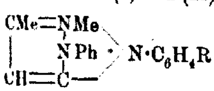
[With F. Kisse.]—5-p-*Tolylimino*-1-*phenyl*-3-*methylpyrazolone*,

$$C_7H_7\cdot N{:}C\Big<\begin{matrix}NPh\cdot N\\ \quad\ \ \| \\ CH_2-CMe\end{matrix},$$

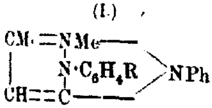
m. p. 109°, is prepared by heating 2 : 5-*p*-tolylimino-1-phenylpyrine hydriodide (following abstract) under 15—20 mm. pressure, or, better, by heating antipyrine chloride and *p*-toluidine (2 mols.) at 200°. Its 4-*oximino*-derivative, m. p. 117°, dark green leaflets, forms a reddish-yellow *hydrochloride*, $C_{17}H_{16}ON_4,HCl$, m. p. 152°, and yields by reduction 4-*amino*-5-p-*toluidino*-1-*phenyl*-3-*methylpyrazole*, m. p. 131° (*hydrochloride*, m. p. 241—242°; *acetyl* derivative, m. p. 193°; *azoimido*-compound, m. p. 111—112°). 4-*Phenyl*-3-p-*tolyl*-6-*methyldihydropyrazofurazan*, $N\Big<\begin{matrix}NPh\cdot C\cdot N(C_7H_7)\\ \| \\ CMe\cdot C\cdot NH\text{———}\end{matrix}\Big>O$, obtained by intramolecular change from the preceding oximino-compound, forms yellow needles, m. p. 176°. 5-*p*-Tolylimino-1-phenyl-3-methylpyrazolone condenses with benzaldehyde and with anisaldehyde in the presence of zinc chloride to form the *benzylidene* and *anisylidene* derivatives, m. p. 163° and 184° respectively.

5-*Anilo*-1-p-*tolyl*-3-*methylpyrazolone*, m. p. 106°, and the corresponding *o-tolyl* compound, m. p. 131°, are obtained by heating the hydriodides of the respective tolylanilopyrines (following abstract). 5-*Methylanilino*-1-p-*tolyl*-3-*methylpyrazole*, m. p. 96°, forms a *hydrochloride*, m. p. 133·5°, and *platinichloride*, m. p. 189°. 5-*Methylanilino*-1-*o-tolyl*-3-*methylpyrazole* has m. p. 67°. 5-*Acetylanilino*-1-p-*tolyl*-3-*methylpyrazole*, $NAcPh\cdot C\Big<\begin{matrix}N(C_7H_7)\cdot N\\ \quad\quad\quad\ \| \\ CH\text{———}CMe\end{matrix}$, and the corresponding *benzoyl* derivative have m. p. 84° and 114° respectively. C. S.

Substituted Iminopyrines. August Michaelis (*Annalen*, 1911, 385, 44—102. Compare preceding abstract).—The chief object of the research is an investigation of various iminopyrines and their derivatives, in order to show that the substances represented by the constitutions (I) and (II) are isomeric and not identical.



(I.)



(II.)

[With Friedrich Walter.]—5-*Chloro*-1-*phenylpyrazole*-3-*carboxylic acid*,

$$CO_2H\cdot C\Big<\begin{matrix}N-NPh\\ | \\ CH{:}CCl\end{matrix},$$

m. p. 158° (*ethyl* ester, m. p. 46°; *chloride*, m. p. 96°), is obtained by heating ethyl 1-phenyl-5-pyrazolone-3-carboxylate with phosphoryl chloride and benzene at 160—170°. The action of chlorine or bromine on its acetic acid solution yields

4 : 5-*dichloro*-1-*phenylpyrazole*-3-*carboxylic acid*, m. p. 214°, and 5-*chloro*-4-*bromo*-1-*phenylpyrazole*-3-*carboxylic acid*, m. p. 222°, respectively. When heated at 200—210°, the chlorophenylpyrazolecarboxylic acid yields 5-chloro-1-phenylpyrazole, which is also conveniently prepared by heating 1-phenyl-5-pyrazolone and phosphoryl chloride at 140—150°. The bromination of 5-chloro-1-phenylpyrazole in acetic acid yields 5-*chloro*-4-*bromo*-1-*phenylpyrazole*, m. p. 65°; 4 : 5-*dichloro*-1-*phenylpyrazole*, m. p. 48°, which cannot be prepared in a similar manner, is obtained by heating 5-chloro-1-phenylpyrazole and phosphorus pentachloride at 150—160°. 3 : 4 : 5-*Trichloro*-1-*phenylpyrazole*, m. p. 82°, is prepared by chlorinating Michaelis and Rohmer's 3 : 5-dichloro-1-phenylpyrazole in chloroform or by heating it with phosphorus pentachloride at 150°. 3 : 5-*Dichloro*-4-*bromo*-1-*phenylpyrazole*, m. p. 85°, is prepared by brominating the dichlorophenylpyrazole. 3 : 5-*Dibromo*-1-*phenylpyrazole*, m. p. 50°, prepared by heating 3-hydroxy-1-phenyl-5-pyrazolone (Michaelis and Schenk, Abstr., 1907, i, 564) with phosphoryl bromide at 120—130°, yields 3 : 4 : 5-*tribromo*-1-*phenylpyrazole*, m. p. 122°, by bromination in boiling acetic acid.

5-*Chloro*-1-*phenylpyrazole* 2-*methiodide*, $NPh<\begin{matrix}CCl=CH\\ N(MeI)\cdot CH\end{matrix}$, m. p. 161° (decomp.), is obtained from its constituents and a little methyl alcohol at 100°. The corresponding *methochloride*, m. p. 147°, forms a *platinichloride*, $2C_{10}H_{10}N_2Cl,PtCl_6,H_2O$, m. p. 207°, and a *picrate*, m. p. 106°. The *ethiodide*, m. p. 209°, *ethochloride*, m. p. 181° (*platinichloride*, m. p. 217°), and *propiodide*, m. p. 156° (decomp.), are also mentioned.

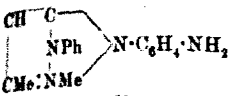
2 : 5-*Anilo*-1-*phenyl*-2-*methylpyrazole*, $\begin{matrix}CH:NMe\\ |\quad NPh\\ CH:C\end{matrix}>NPh$, m. p. 128°, prepared by the general method of heating 5-chloropyrazole-2-alkyliodides and primary aromatic bases (preceding abstract), forms a *hydrochloride*, *platinichloride*, m. p. 177°, *hydriodide*, m. p. 161° (identical with 5-anilo-1-phenylpyrazolone-2-methiodide [preceding abstract]), *thiocyanate*, m. p. 137°, *picrate*, m. p. 104°, *methiodide*, $\begin{matrix}CH\cdot C(MeI)\\ CH:C(NPhMe)\end{matrix}>NPh$, m. p. 124—125°, *ethiodide*, m. p. 146°, and *benzoyl iodide*, $C_{16}H_{15}N_3,C_6H_5\cdot COI$, m. p. 108°. 2 : 5-*Anilo*-1-*phenyl*-2-*ethylpyrazole*, m. p. 155°, and 2 : 5-*anilo*-1-*phenyl*-2-*propylpyrazole*, m. p. 124·5°, are prepared by the general method; the former forms a *platinichloride*, m. p. 197°, *hydriodide*, m. p. 149°, *picrate*, m. p. 172°, and *methiodide*, m. p. 119°, whilst the *platinichloride* and *hydriodide* of the latter have m. p. 195° and 165° respectively.

[With ERICH WURL and FELIX DOEPMANN.]—2 : 5-m-*Nitroanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (2 : 5-m-*nitroanilopyrine*) (annexed formula), m. p. 114°, garnet-red crystals, and 2 : 5-p-*nitroanilopyrine*, m. p. 129°, dark red crystals with a green shimmer, are obtained from antipyrine chloride and the nitroanilines

$$\begin{matrix}CH=C\\ |\quad NPh\\ CMe:NMe\end{matrix}>N\cdot C_6H_4\cdot NO_2$$

by the general method. The former forms a *platinichloride*, $(C_{17}H_{16}O_2N_4)_2,H_2PtCl_6,3\frac{1}{2}H_2O$, m. p. 204° (decomp.), *hydriodide*, m. p. 164°, *methiodide*, m. p. 144°, *acetyl iodide*, m. p. 196° (decomp.), and *benzoyl iodide*, m. p. 178°, whilst 2 : 5-*p*-nitroanilopyrine forms a *platinichloride*, m. p. 217°, *hydriodide*, m. p. 198° (decomp.), and *methiodide*, m. p. 194° (decomp.) (compare this vol., i, 232, for the isomeric nitroanilopyrines and their derivatives). 2 : 5-o-*Nitro*-p-*tolylimino*-1-*phenyl*-2 : 3-*dimethylpyrazole* (formula I), m. p. 100°, stout, red crystals, forms a *platinichloride*, m. p. 131°, and *picrate*, m. p. 145°.

(I.)



(II.)

2 : 5-m-*Aminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole* (formula II), m. p. 45—50°, can be prepared by reducing the nitro-compound, but is far more conveniently obtained by heating antipyrine chloride and acetyl-*m*-phenylenediamine at 125—130° and hydrolysing the resulting acetyl derivative, m. p. 212°. It forms a *dihydrochloride*,

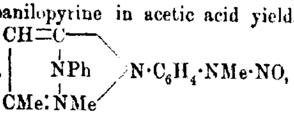
$$C_{17}H_{18}N_4,2HCl,$$

decomp. 260°, *platinichloride*, decomp. 227°, *benzoyl* derivative, m. p. 172°, and *benzoyl iodide*, m. p. 218°, the *hydrochloride*,

$$C_{24}H_{23}ON_4I,HCl,$$

of which has m. p. 222°. 2 : 5-p-*Aminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 112°, prepared by similar methods as the meta-isomeride, forms a *dihydrochloride*, m. p. 245°, and an *acetyl* derivative, m. p. 196°, the *hydriodide* of which has m. p. 151°.

as-Dimethyl-*p*-phenylenediamine and antipyrine chloride react best at 125° to form 2 : 5-p-*dimethylaminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 120°, green plates or greenish-yellow prisms, which is a very strong base, absorbs carbon dioxide, and forms two series of salts, according as one equivalent of an acid combines with the dimethylamino-group, or as yet another equivalent breaks the bridge; the former salts are green, faintly alkaline, and contain H_2O, whilst the latter are colourless, faintly acidic, and anhydrous. The *dihydrochloride*, m. p. 224°, *dihydriodide*, m. p. 208°, *hydrochloride*, m. p. 116°, *hydriodide*, m. p. 72—73°, *dimethiodide*, m. p. 205°, and *methiodide*, m. p. 153°, are described. The action of sodium nitrite (3 mols.) on 2 : 5-*p*-dimethylaminoanilopyrine in acetic acid yields formaldehyde and the *nitrosoamine*,

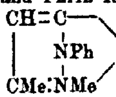


m. p. 169°, orange-yellow leaflets, which is converted by reduction into 2 : 5-p-*methylaminoanilo*-1-*phenyl*-2 : 3-*dimethylpyrazole*, m. p. 143°, sulphur-yellow needles (*acetyl* derivative, m. p. 142°). The *nitrosoamine*, m. p. 164°, dark red needles (*hydriodide*, m. p. 192°), of 4-nitro-2 : 5-*p*-methylaminoanilo-1-phenyl-2:3-dimethylpyrazole is obtained by passing nitrous fumes into an alcoholic solution of the preceding nitrosoamine containing a little acetic acid.

m-*Phenylenebis-2 : 5-imino-1-phenyl-2 : 3-dimethylpyrazole* (annexed formula), m. p. 204°, yellowish-white crystals, is obtained by heating m-phenylenediamine and antipyrine chloride at 130—135°, and forms a

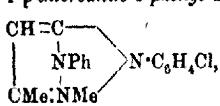
platinichloride, decomp. 300°, *dihydriodide*, m. p. 203°, and *dimethiodide*, m. p. 154°.

[With WILHELM THOMAS and FRITZ ISBERT.]—2 : 5-p-*Chloroanilo-1-phenyl-2 : 3-dimethylpyrazole*,



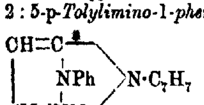
m. p. 78°, yellow prisms, is obtained by heating *p*-chloroaniline (2 mols.) and antipyrine chloride or 5-chloro-1-phenyl-3-methylpyrazole-2-methiodide on the water-bath. It forms a *hydrochloride, platinichloride*, m. p. 89° (decomp. in its $6H_2O$ of crystallisation), *hydriodide*, m. p. 180°, *picrate*, m. p. 147°, *methiodide*, m. p. 192°, *ethiodide*, m. p. 172°, and *benzoyl iodide*, m. p. 183°. 2 : 5-m : p-*Dichloroanilo-1-phenyl-2 : 3-dimethylpyrazole*, a yellow oil (*picrate*, m. p. 152°; *methiodide*, m. p. 191°), 2 : 5-p-*bromoanilo-1-phenyl-2 : 3-dimethylpyrazole*, m. p. 81° (*platinichloride*, m. p. 115°; *hydriodide*, m. p. 206°; *picrate*, m. p. 159°; *methiodide*, m. p. 193°; *ethiodide*, m. p. 176°), and 2 : 5-m-*bromoanilo-1-phenyl-2 : 3-dimethylpyrazole*, a yellow oil (*platinichloride*, m. p. 211°; *hydriodide*, m. p. 205°; *picrate*, m. p. 190°; *methiodide*, m. p. 133°; *ethiodide*, m. p. 118°), have also been prepared.

1-p-*Chlorophenyl-3-methyl-5-pyrazolone*, m. p. 88°, is obtained by heating equal molecular quantities of *p*-chlorophenylhydrazine and ethyl acetoacetate in 50% acetic acid at 100°. Its *methiodide*, m. p. 233° (decomp.), reacts with an excess of aniline at 110° to form 1-p-*chloroanilo-1-phenyl-2 : 3-dimethylpyrazole* (annexed formula), m. p. 96°, yellow needles (*hydrochloride*, m. p. 200°; *platinichloride*, m. p. 199°; *hydriodide*, m. p. 189°; *picrate*, m. p. 192°; *methiodide*, m. p. 70° [hydrated] or 159° [anhydrous]; *methochloride*, m. p. 155°).



1-p-*Bromoanilo-1-phenyl-2 : 3-dimethylpyrazole*, m. p. 119°, forms a *hydrochloride*, m. p. 202—203°, *platinichloride*, decomp. 202°, *aurichloride*, m. p. 166°, *hydriodide*, m. p. 176°, *picrate*, m. p. 193°, *methochloride*, m. p. 157°, and *methiodide*, m. p. 101° (hydrated) and 158° (anhydrous).

[With WALDEMAR MENTZEL.]—The 2 : 5-tolylimino-1-phenyl-2 : 3-dimethylpyrazoles have been prepared by the general method from antipyrine chloride and *o*- or *p*-toluidine (2 mols.) at 125°. 2 : 5-p-*Tolylimino-1-phenyl-2 : 3-dimethylpyrazole* (annexed formula), m. p. 106°, white leaflets, forms a *hydrochloride*, m. p. 207°, *platinichloride*, m. p. 138°, *hydriodide*, m. p. 166°, *picrate*, m. p. 144°, *methiodide*, m. p. 187°, *acetyl iodide*, m. p. 166°, and *benzoyl iodide*, m. p. 207°. 2 : 5-o-*Tolyl-*



anino-1-phenyl-3 : 3-dimethylpyrazole, m. p. 69°, forms a *hydriodide*, m. p. 137°, and *methiodide*, m. p. 192°. The isomeric 1-*p*- and *o*-tolyl-anilopyrines have been prepared from aniline (2 mols.) and 1-*p*- or *o*-tolylantipyrine chloride at 125°. 2 : 5-*Anilo*-1-*p*-*tolyl*-3 : 3-*dimethylpyrazole*, m. p. 106°, forms a *platinichloride*, m. p. 210°, *hydriodide*, m. p. 165·5°, *picrate*, m. p. 169°, *methiodide*, m. p. 175°, *acetyl iodide*, m. p. 206°, and *benzoyl iodide*, m. p. 147°, whilst 2 : 5-*anilo*-1-*o*-*tolyl*-3 : 3-*dimethylpyrazole*, m. p. 129°, yields a *hydriodide*, m. p. 196°, and *methiodide*, m. p. 167°. C. S.

Ethyl Arylazoacetonedicarboxylates and their Isomeric Condensation Products with Hydrazines. CARL BÜLOW and HERMANN GÖLLER (*Ber.*, 1911, **44**, 2835—2847).—The reaction between a diazonium salt and ethyl acetonedicarboxylate in cold aqueous alcohol in the presence of sodium acetate yields *ethyl arylazoacetonedicarboxylates*, $R\cdot N_2\cdot CH(CO_2Et)\cdot CO\cdot CH_2\cdot CO_2Et$, which are yellow, crystalline substances soluble in dilute alkalis: R = Ph, m. p. 48·5°; $R = o\text{-}C_7H_7$, m. p. 80—85°, decomp. 195°; $R = p\text{-}C_7H_7$, m. p. 81—81·5°; $R = m\text{-}C_6H_3Me_2$, m. p. 71—72°; $R = o\text{-}C_6H_4\cdot CO_2H$, m. p. 145—146°. These substances react with phenylhydrazine in glacial acetic acid at the ordinary temperature to form *ethyl 5-hydroxy-1-phenylpyrazole-3-glyoxylate-arylhydrazones*,

$$\begin{array}{l}NPh\cdot N\\ OH\cdot C{=}CH\end{array}\!\!>\!C\cdot C(CO_2Et){:}N\cdot NHR\,;$$

R = Ph, m. p. 137—138°; $R = o\text{-}C_7H_7$, m. p. 171° (decomp.); $R = p\text{-}C_7H_7$, m. p. 170—171° (decomp.); $R = m\text{-}C_6H_3Me_2$, m. p. 151°; $R = o\text{-}C_6H_4\cdot CO_2H$, m. p. 218—219° (decomp.). These compounds, which are yellow and crystalline, are given the constitution stated, because they respond to the Bülow reaction, and are soluble in dilute alkalis or aqueous piperidine. In a similar manner, the ethyl arylazoacetonedicarboxylates react with 60% hydrazine hydrate to form yellow, crystalline ethyl 5-hydroxypyrazole-3-glyoxylate-arylhydrazones,

$$\begin{array}{l}NH{-}{-}{-}N\\ C(OH){:}CH\end{array}\!\!>\!C\cdot C(CO_2Et){:}N\cdot NHR;$$ R = Ph, m. p. 170—171° (decomp.); $R = o\text{-}C_7H_7$, m. p. 162°; $R = p\text{-}C_7H_7$, m. p. 180—181° (decomp.); $R = m\text{-}C_6H_3Me_2$, m. p. 207—208° (decomp.); $R = o\text{-}C_6H_4\cdot CO_2H$, decomp. 255°, darkening at 235°.

The two preceding groups of compounds are isomeric with the ethyl 4-arylazo-5-hydroxy-1-phenylpyrazole-3-acetates or ethyl 4-arylazo-5-hydroxypyrazole-3-acetates obtained by condensing ethyl 5-hydroxy-1-phenylpyrazole-3-acetates or ethyl 5-hydroxypyrazole-3-acetates respectively with diazonium salts in the presence of sodium acetate; thus ethyl 5-hydroxy-1-phenylpyrazole-3-acetate and *p*-toluenediazonium chloride yield *ethyl 4-p-tolueneazo-5-hydroxy-1-phenylpyrazole-3-acetate*, $NPh\!<\!\begin{array}{l}N{=\!=}C\cdot CH_2\cdot CO_2Et\\ C(OH){:}C\cdot N_2\cdot C_7H_7\end{array}$, m. p. 132—134°, orange needles, which is soluble in dilute alkalis or aqueous piperidine; its constitution is proved by the fact that the *acid*, obtained by its hydrolysis by 10% alkali, loses carbon dioxide at 175—180°, yielding Lapworth's 4-*p*-tolueneazo-5-hydroxy-1-phenyl-3-methylpyrazole. The constitution of

ethyl 4-*p*-nitrobenzeneazo-5-hydroxy-1-phenylpyrazole-3-acetate, prepared by the preceding or by Bülow and Höpfner's method (Abstr., 1901, i, 239), has been similarly proved by converting the substance into 4-*p*-nitrobenzeneazo-5-hydroxy-1-phenyl-3-methylpyrazole. C. S.

Quadriurates. WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, 75, 13—18. Compare Kohler, this vol., i, 243, 690; also Ringer, Abstr., 1910, ii, 838).—It is considered that the non-existence of quadriurates has not been proved as yet. The possibility of the formation of mixed crystals of urates and uric acid is suggested. On cooling such a mixture, the solid would remain in presence of its mother liquor for a time, although not in equilibrium with it, and still less in equilibrium with water. In time, decomposition and liberation of part of the uric acid would take place. The mixed crystals formed on evaporation at a constant temperature are in equilibrium with the mother liquors; they therefore do not decompose when kept, and decompose only very slowly in presence of water at the same temperature. Such substances would correspond in composition with the quadriurates without being true chemical compounds. E. F. A.

Benziminazoles and Benzoxazoles and Azo-dyes Derived Therefrom. OTTO KYM and S. KOWARSKI (*Ber.*, 1911, 44, 2919—2932. Compare Abstr., 1904, i, 453).—The effect on the colour and affinity for vegetable fibres of an increasing number of amino-groups in azo-dyes of this class has been investigated already, and in this paper the effect in this direction of introducing (*a*) a second iminazole group or (*b*) a second oxazole group, is shown to be the production of a red tone in the dye, with no increase in the affinity for cotton.

3-*Nitro*-1 : 4-*di*-p-*nitrobenzoyl*-p-*phenylenediamine*,

$$NO_2\cdot C_6H_3(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2,$$

m. p. above 305°, prepared by the action of *p*-nitrobenzoyl chloride on either nitro-*p*-phenylenediamine or nitrodiacetyl-*p*-phenylenediamine, crystallises from pyridine on adding hot alcohol in glancing, golden-yellow leaflets. On nitration with fuming nitric acid, it gives 2 : 3-*dinitro*-1 : 4-*di*-p-*nitrobenzoyl*-p-*phenylenediamine*, m. p. 262°, which may also be obtained by the action of *p*-nitrobenzoyl chloride on dinitrodiacetyl-*p*-phenylenediamine. This crystallises from acetone on addition of water in small, yellow needles, is much more soluble in organic solvents than the mononitro-compound, and on reduction with tin and hydrochloric acid furnishes the corresponding 2 : 5-*di*-p-*aminophenyl*-o-*benzdi-iminazole*,

$$NH_2\cdot C_6H_4\cdot C\begin{matrix}\nearrow NH\cdot C\cdot CH\cdot CH\cdot C\cdot NH \searrow\\ \searrow N\text{—}C\text{————}C\text{—}N \nearrow\end{matrix}C\cdot C_6H_4\cdot NH_2,$$

which sinters at 230°, losing water of crystallisation, and then melts at 255°; it crystallises from pyridine on addition of water in bright brown, glancing needles, and shows a bluish-violet fluorescence in all solutions. The *diacetyl* derivative is colourless and practically insoluble in all solvents.

4 : 6-*Dinitroresorcinyl di*-p-*nitrobenzoate*, m. p. 178°, prepared by treating dinitroresorcinol with *p*-nitrobenzoyl chloride, crystallises in

slender, yellowish-brown needles from boiling acetic acid on addition of water, and is insoluble in acetone or pyridine, but appears to undergo change in the latter solvent, since addition of water causes the separation of an intensely yellow jelly. On reduction with stannous chloride, tin, and hydrochloric acid, it furnishes a 5% yield of 1 : 5-*di-p-aminophenylbenzdioxazole*,

$$NH_2\cdot C_6H_4\cdot C{<}^{O}_{N}{>}C_6H_2{<}^{O}_{N}{>}C\cdot C_6H_4\cdot NH_2,$$

which sinters at 170° and remains unchanged on further heating, crystallises from hot acetone on addition of water in small, brown needles, and shows a bluish-violet fluorescence in alcohol. The same substance was obtained in larger yield in the following series of reactions.

When 4 : 6-diaminoresorcinol hydrochloride is heated with *p*-nitrobenzoyl chloride in xylene solution, *di-p-nitrobenzoyldiaminoresorcinol*, $C_6H_2(OH)_2(NH\cdot CO\cdot C_6H_4\cdot NO_2)_2$, is obtained as an orange-coloured, insoluble, sandy powder, which does not melt at 300°, but on heating at 260—270° is converted into 1 : 5-*di-p-nitrophenylbenzdioxazole*, which alone is formed if the initial reaction is carried out in nitrobenzene solution instead of xylene. This has m. p. above 300°, forms small, bright yellow needles, and is insoluble in acids or alkalis, but can be recrystallised from nitrobenzene. On reduction by heating with zinc dust and acetic acid, it gave the corresponding 1 : 5-di-*p*-aminophenylbenzdioxazole described above.

The diaminobenzdi-iminazole and diaminobenzdioxazole bases here described were diazotised and coupled with aminonaphtholdisulphonic acid, β-naphtholdisulphonic acid, and α-naphthol, and gave in each case dyes which on cotton furnished colours distinctly redder in shade than those given by the corresponding products from the monoiminazole and mono-oxazole respectively. T. A. H.

Azoxy-compounds. Angelo Angeli and Luigi Alessandri (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 170—176. Compare this vol., i, 817).—The *p*-nitroazoxybenzene of Zinin is unaltered when treated with nitric acid (D 1·48) for four minutes at room temperature (27°), whilst under these conditions the compound of m. p. 148° (now given as 149°), previously described, yields 4 : 4′-dinitroazoxybenzene, which is only formed from Zinin's compound when the action of the nitric acid is prolonged. Both substances remain unaltered when treated with bromine in glacial acetic acid, but if they are mixed with a little iodine and added to bromine, Zinin's compound is unacted on, whilst from the other a *bromo*-derivative is produced, crystallising in yellow prisms, m. p. 199°. Azoxybenzene in similar circumstances gives a *bromo*-derivative, m. p. 75°. R. V. S.

Action of Phosphorus Pentachloride on the Azoxy-compounds. G. Charrier and G. Ferreri (*Atti R. Accad. Sci. Torino*, 1911, 46, 1009—1023).—The authors have studied the action of phosphorus pentachloride on the azoxy-compounds obtained by uniting β-naphthol with *o*- and *p*-methoxyphenyldiazonium chloride, and with *o*- and *p*-ethoxyphenyldiazonium chloride. They find that in the case of

the compounds from *p*-anisidine and *p*-phenetidine, the hydroxy-group is substituted by chlorine. The derivatives of *o*-anisidine and *o*-phenetidine, however, behave differently; hydrogen chloride and methyl or ethyl chloride are evolved, and a compound containing phosphorus and chlorine is obtained, for which the formula $\begin{matrix} N\cdot C_6H_4-O \\ \| \\ N\cdot C_{10}H_6\cdot O \end{matrix}\!\!>PCl_3$ is suggested. This substance yields *o*-hydroxybenzeneazo-β-naphthol when treated with water. In addition, all the azoxy-compounds give small quantities of infusible substances containing phosphorus.

o-*Methoxybenzeneazo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4\cdot OMe$, forms yellowish-red needles, m. p. 178°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration.

o-*Ethoxybenzeneazo-β-naphthol*, $C_{18}H_{16}O_2N_2$, crystallises in minute, orange-red leaves, m. p. 138°. It gives a reddish-violet coloration with concentrated sulphuric acid.

o-Hydroxybenzeneazo-β-naphthol crystalises in three forms: (1) green tablets (from ethyl alcohol and ethyl acetate); (2) in crusts of small, red needles (from benzene and toluene); (3) red needles with a golden lustre (from methyl alcohol). The last two forms change into the first in contact with alcohol or on heating. The *sodium* salt, $C_{16}H_{11}O_2N_2Na,3H_2O$, and the *potassium* salt, $C_{16}H_{11}O_2N_2K,1\frac{1}{2}H_2O$, which both crystallise in green scales, were prepared. The *acetyl* derivative, $C_{18}H_{14}O_3N_2$, forms ruby-red needles, m. p. 153°. The *benzoyl* derivative, $C_{23}H_{16}O_3N_2$, forms small, orange-yellow needles, m. p. 216°. The *benzyl* derivative, $C_{23}H_{18}O_2N_2$, crystallises in small, red needles, m. p. 152—153°.

p-*Methoxybenzeneazo-β-naphthol*, $C_{17}H_{14}O_2N_2$, forms red needles, m. p. 137°. It dissolves in concentrated sulphuric acid, giving a reddish-violet coloration, and is reprecipitated on addition of water. When it is heated with an equimolecular quantity of phosphorus pentachloride on the water-bath, 1-p-*methoxybenzeneazo-2-chloronaphthalene*, $C_{10}H_6Cl\cdot N\colon N\cdot C_6H_4\cdot OMe$, is produced; it crystallises in small, orange-red prisms or lustrous, reddish-yellow scales, m. p. 87°. It gives a reddish-violet coloration with concentrated sulphuric acid. On reduction with zinc and acetic acid, it yields *p*-anisidine and 2-chloro-1-naphthylamine, of which the *monoacetyl* derivative, $C_{12}H_{10}ONCl$, crystallises in colourless needles, m. p. 191°, and the *diacetyl* derivative, $C_{14}H_{12}O_2NCl$, forms colourless prisms, m. p. 88°. With nitrous acid, 2-chloro-1-naphthylamine yields in solution 2-*chloro-1-naphthyldiazonium chloride*, which reacts with β-naphthylamine to form 2-*chloro-1-naphthaleneazo-2'-naphthylamine*, $C_{10}H_6Cl\cdot N\colon N\cdot C_{10}H_6\cdot NH_2$, which crystallises in red needles, m. p. 125°; this substance dissolves in concentrated sulphuric acid with production of an intense blue coloration. 2-Chloro-1-naphthyldiazonium chloride and β-naphthol yield 2-*chloro-1-naphthaleneazo-β-naphthol*, $C_{10}H_6Cl\cdot N\colon N\cdot C_{10}H_6\cdot OH$, which forms minute, red needles, m. p. 177°, and gives a bluish-violet coloration with concentrated sulphuric acid.

p-*Ethoxybenzeneazo-β-naphthol*, $OH\cdot C_{10}H_6\cdot N\colon N\cdot C_6H_4\cdot OEt$, crystallises in red needles, m. p. 132°; it dissolves in concentrated sulphuric acid, giving a reddish-violet coloration, and is reprecipitated on addition of water. 1-p-*Ethoxybenzeneazo-2-chloronaphthalene*,

$C_{13}H_{10}ON_4Cl$, crystallises in orange-yellow leaflets, m. p. 94°, and gives a violet coloration with concentrated sulphuric acid. R. V. S.

Behaviour of Some Nitroazo-derivatives Towards Phenylhydrazine. C. GASTALDI (*Gazzetta*, 1911, **41**, ii, 319—324. Compare Ponzio, Abstr., 1909, i, 443).—o-*Nitrobenzoylazobenzene*,

$$NO_2\cdot C_6H_4\cdot CO\cdot N:NPh,$$

is obtained by the action of nitrous anhydride on an ethereal suspension of *o*-nitrobenzoylphenylhydrazine; it crystallises in red needles, m. p. 89°, and is reduced by phenylhydrazine to *o*-nitrobenzoylphenylhydrazine.

m-Nitrobenzoylphenylhydrazine, $NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NHPh$, is obtained by acting on an ethereal solution of phenylhydrazine with *m*-nitrobenzoyl chloride; it forms yellow laminæ, m. p. 158° (Autenrieth gave 205°; compare Abstr., 1901, i, 186).

m-*Nitrobenzoylazobenzene*, $C_{13}H_9O_3N_3$, crystallises in dark red laminæ, m. p. 117°, and is reduced to *m*-nitrobenzoylphenylhydrazine by phenylhydrazine.

p-*Nitrobenzoylazobenzene*, $C_{13}H_9O_3N_3$, forms small, red laminæ, m. p. 136°, and is similarly reduced by phenylhydrazine.

o-*Nitrobenzoyl*-p-*bromophenylhydrazine*,

$$NO_2\cdot C_6H_4\cdot CO\cdot NH\cdot NH\cdot C_6H_4Br$$

(from *p*-bromophenylhydrazine and *o*-nitrobenzoyl chloride), crystallises in colourless needles tinged with yellow, and has m. p. 193°. When oxidised it gives o-*nitrobenzoylazo*-p-*bromobenzene*, m. p. 119—120°, which is, however, not pure.

m-*Nitrobenzoyl*-p-*bromophenylhydrazine*, $C_{13}H_{10}O_3N_3Br$, crystallises in pale yellow needles, m. p. 198°. m-*Nitrobenzoylazo*-p-*bromobenzene*, $C_{13}H_8O_3N_3Br$, forms bronze-coloured laminæ, m. p. 124°, and is reduced to *m*-nitrobenzoyl-*p*-bromophenylhydrazine by phenylhydrazine.

p-*Nitrobenzoyl*-p-*bromophenylhydrazine*, $C_{13}H_{10}O_3N_3Br$, crystallises in yellow needles, m. p. 194°. p-*Nitrobenzoylazo*-p-*bromobenzene*,

$$C_{13}H_8O_3N_3Br,$$

crystallises in bronze-coloured laminæ, m. p. 153°, and is reduced to *p*-nitrobenzoyl-*p*-bromophenylhydrazine by phenylhydrazine.

R. V. S.

Preparation of Bromonaphthalene-1-diazo-2-oxide-4-sulphonic Acid. CHEMISCHE FABRIK VORM. SANDOZ (D.R.-P. 236656).—When naphthalene-1-diazo-2-oxide-4-sulphonic acid is dissolved in concentrated sulphuric acid or chlorosulphonic acid, treated with bromine, and heated at 60—65°, bromination takes place, yielding *bromonaphthalene*-1-*diazo*-2-*oxide*-4-*sulphonic acid*, decomp. 180°; the *zinc* salt forms glistening, greenish-yellow needles.

F. M. G. M.

Nitrogen Chains: Diazohydrazides from Diazotetrazole. KARL A. HOFMANN and HEINRICH HOCK (*Ber.*, 1911, **44**, 2946—2956. Compare Abstr., 1910, i, 446, 547; this vol., i, 359).—Diazotetrazoleaminoguanidine (guanyltetrazyltetrazen),

$$NH:C(NH_2)\cdot NH\cdot NH\cdot N:N\cdot CN_4H,H_2O,$$

prepared as already described (Abstr., 1910, i, 446), crystallises in yellow, doubly refractive needles, is stable in air at 25—35°, and decomposes with slight explosion at 142°. It is acid to litmus, but dissolves in dilute nitric acid. It does not react with mercuric oxide or benzaldehyde, but Fehling's solution furnishes copper diazotetrazole (?) as a brown powder. Sodium hydroxide decomposes it into cyanamide, ammonia, and tetrazylazoimide. When heated with dilute sulphuric or nitric acid, cyanogen and nitrogen are evolved, and the residue contains aminoguanidine and its decomposition products, as well as aminotetrazolic acid. The *periodide*, $C_2H_2N_{14}I_7$, which forms brown to black, pleochroic, cubical crystals, explodes gently when heated, but very violently in contact with nitric acid and silver nitrate.

Diazotetrazole-semicarbazide, $NH_2\cdot CO\cdot NH\cdot NH\cdot N:N\cdot CN_4H,H_2O$, m. p. 122°, obtained by adding diazotetrazole to semicarbazide hydrochloride in aqueous solution in presence of sodium acetate, forms colourless, doubly-refractive crystals when dilute nitric acid is added to its solution in alkali. It is acid to litmus, and is only slowly decomposed by alkali, forming tetrazylazoimide and carbamide. The same products result from heating the substance with water or dilute acids.

The decompositions of these two substances are in harmony with the constitution assigned to them (compare Curtius, Abstr., 1893, i, 463; Wohl, Abstr., 1893, i, 509; Thiele and Marais, Abstr., 1893, i, 440).

Diazotetrazolebenzylideneaminoguanidine,

$$NH:C(NH_2)\cdot N(C_7H_6)\cdot N\cdot N:N\cdot CN_4H,$$

obtained by admixture of its components in acetic acid, is an orange-red substance, decomposes at 132°, and crystallises in groups of needles from alcohol by evaporation of its solution under reduced pressure. It is decomposed by acids, yielding nitrogen, cyanogen, benzaldehyde, and hydrazine. With concentrated sodium hydroxide solution it gives a *sodium* derivative, orange-red needles. *Diazotetrazolephenylhydrazide*, $NH_2\cdot NPh\cdot N:N\cdot CN_4H$, obtained by interaction of phenylhydrazine with diazotetrazole in acetic acid, separates from methyl alcohol on adding ether, in orange-red crystals, gives a brownish-red *sodium* derivative, and is decomposed by acids, yielding nitrogen, cyanogen, and phenylhydrazine. The mode of decomposition of these two compounds indicates that they are α-hydrazides, their behaviour with acids and alkalis clearly distinguishing them from the β-hydrazides represented by the first two (compare Wohl and Schiff, Abstr., 1900, i, 706).

Bisdiazotetrazolehydrazide, $HN_4C\cdot N:N\cdot NH\cdot NH\cdot N:N\cdot CN_4H$, obtained by adding hydrazine hydrochloride to diazotetrazole hydrochloride, both being in strongly cooled solution, occurs in doubly refractive spangles, and can be kept for a month in a desiccator at 25°, but explodes with great violence when pressed with a glass rod or heated to 90°. It is decomposed by acids, yielding nitrogen (5 atoms), cyanogen, ammonia, and tetrazylazoimide, but no hydrazine. Concentrated sodium hydroxide solution gives a *sodium* derivative, as intensely yellow, doubly refractive plates, which in water decomposes, giving nitrogen, tetrazylazoimide, and aminotetrazole, but no

ammonia. These reactions are in harmony with the constitution assigned to the substance, as are also its acid reaction and non-reactivity with benzaldehyde. With Fehling's solution gas is evolved, the solution becomes brownish-yellow, and, on warming, reddish-brown flocks are deposited, probably of a copper derivative or diazotetrazole.

Guanidine and dicyanodiamidine react with diazotetrazole to form salts of diazoaminotetrazolic acid (compare Abstr., 1910, i, 547). The *dicyanodiamidine* salt forms yellow groups of microscopic needles, and dissolves in sodium hydroxide solution, from which alcohol precipitates the *sodium* salt, $C_2N_{11}Na_3,H_2O$, doubly refractive, yellow needles. The well crystallised *barium* salt, $(C_2N_{11})_2Ba_3,8H_2O$, may be obtained from this by double decomposition. T. A. H.

A New Method of Preparing Diazoamino-compounds, and a New Reaction for Nitrous Acid. WILHELM VAUBEL (*Chem. Zeit.*, 1911, 133, 1238).—Sodium nitrite, in aqueous solution, acts on the salts of aromatic amines with mineral acids to form diazoamino-benzene and its derivatives. Aniline hydrochloride and sodium nitrite yield diazoaminobenzene, the best yield of the latter being obtained when the proportions taken are 1 mol. of aniline hydrochloride and ½ mol. of sodium nitrite. Hydrochlorides may be replaced by nitrates. Reaction proceeds more slowly when salts of different amines are mixed before addition of the nitrite.

A similar action occurs when solid sodium nitrite is added to an alcoholic solution of the amine salt, and also when the dry salts are intimately mixed. In these cases the reaction can easily become so violent that a portion of the diazoaminobenzene is decomposed.

The reaction may also be used in testing the presence of nitrites in water. The presence of 0·00035% of nitrite could be recognised by the yellow coloration formed on addition of aniline hydrochloride.

H. W.

Losses in the Isolation of Monoamino-acids [from Proteins] by the Ester Method. I. EMIL ABDERHALDEN and ARTHUR WEIL (*Zeitsch. physiol. Chem.*, 1911, 74, 445—471. Compare Osborne and Breese Jones, Abstr., 1910, i, 598).—The isolation of the monoamino-acids obtained on hydrolysing proteins is not a quantitative operation. In the case of glutamic and aspartic acids, the yields obtained, starting from the pure acids, esterifying, and converting the ester into acid again, have been determined. The experiments have been carried out in a variety of ways, and the losses at each stage of the process determined by nitrogen determinations; for the details, the original should be consulted.

Starting from pure aspartic acid, about 40% is lost during the isolation by the ester method; with glutamic acid the loss is 30%. Glutamic acid is usually isolated without the help of the ester method, and the loss in this case will not be larger, but it is considered that the values for aspartic acid previously obtained can be doubled. E. F. A.

Ochrein. FRANCESCO MARINO-ZUCO and IDA FOA (*Gazzetta.*, 1911, 41, ii, 331—336).—Ochrein is the name given by the authors to the

substance containing iron which is obtained when biotoxin acts on blood or hæmoglobin (compare Marino-Zuco and Giuganino, Abstr., 1910, ii, 223). It is prepared by incubating a sterile solution of biotoxin and oxyhæmoglobin for five or six days at 41°, until the absorption spectrum of hæmoglobin is no longer present, and the liquid does not become turbid on heating. The substance is an amorphous, ochre-coloured powder, insoluble in most solvents. The percentage composition of different samples is the same, and corresponds with the formula $C_{288}H_{508}O_{70}N_{79}Fe$. When heated with extremely dilute sodium hydroxide, a very small quantity of the substance dissolves, and the solution shows the spectrum which appears when biotoxin acts on blood (compare Marino-Zuco and Giuganino, *loc. cit.*). R. V. S.

3:5-Di-iodotyrosine from Iodised Protein. III. From Iodocasein. ADOLF OSWALD (*Zeitsch. physiol. Chem.*, 1911, **74**, 290—296).—3:5-Di-iodotyrosine was prepared from iodocasein, but the yield is small, namely, about 1%. Iodocasein contains 10—14% of iodine; of this, only 4—5% is united to tyrosine; the amount obtained represents only about one-tenth of the tyrosine present. W. D. H.

Composition of Different Kinds of Silk. XIII. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, **74**, 427—428).—Silk from the cocoon of *Anapha* contained tyrosine, alanine, and glycine in large quantity, and was similar in composition to other kinds of silk. Silk from *Bombyx mori* and African tussore silk was also qualitatively similar.

Silks as a class are very similar in composition, all consisting mainly of tyrosine, alanine, and glycine. They are not, however, identical, showing differences in the nature and amount of their rarer constituents. E. F. A.

The Proteoses. EDGARD ZUNZ (*Bull. Acad. roy. Belg.*, 1911, 653—734).—The hetero- and prot-albumoses prepared by the methods of Pick, Adler, and Haslam, as well as the synalbumose and thio-albumose of Pick, were prepared in quantity, and a large number of both chemical and physical constants of the preparations were ascertained. The experimental methods are given in full detail, and the analytical results and physical constants are tabulated. Further separations were also attempted by the methods of ultra-filtration (Bechhold) and precipitation by colloids (Michaelis and Rona). It was found that the method of Pick yields products of the most constant composition, and his method of classification of the proteoses appears to be preferable to that suggested by Haslam, although it can be improved in certain details in the technique of precipitation introduced by Haslam. Certain differences in the physiological action of the fractions previously observed by the author are also summarised. S. B. S.

Plastein Formation. A. RAKOCZY (*Zeitsch. physiol. Chem.*, 1911, **75**, 273—281).—The Danilewski reaction is not due to the action of any specific substance, but plastein formation occurs in the case of all proteoclastic enzymes, rennet included. W. D. H.

Nomenclature of Enzymes. HANS VON EULER (*Zeitsch. physiol. Chem.*, 1911, **74**, 13—14).—Enzymes are usually named after the substances they split, for instance, for example, maltase after maltose. This rule is difficult to apply to enzymes which produce syntheses. The suggestion made is that the termination in such cases should be *ese* instead of *ase*, for instance, lipase, lipese. W. D. H.

The Mode of Action of Phosphatese. HANS VON EULER and SIXTEN KULLBERG (*Zeitsch. physiol. Chem.*, 1911, **74**, 15—28).—There is no evidence that the enzyme which synthesises carbohydrate phosphoric acid esters has any splitting action. The term *phosphatese* is suggested (see preceding abstract); it is active in faintly alkaline media, but its stability is small. The ester formed from dextrose and lævulose is optically inactive, and on decomposition by acids or bases yields no optically active products. The enzyme is found in yeast and *Aspergillus*. Two enzymes are really in all probability concerned, one which changes the dextrose or lævulose into an ester-forming carbohydrate, and the second is the phosphatese which builds together the carbohydrate and phosphate ions. W. D. H.

The Electrical Transport of Pepsin. CORNELIS A. PEKELHARING and WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, **75**, 282—289).—Using a commercial preparation of pepsin, Michaelis and Davidsohn (Abstr., 1910, i; 795) drew the conclusion that with acid of a certain strength, the pepsin travelled to both poles; on lessening the strength of acid, it went only to the cathode; with still weaker acid it again went to both poles, and finally with the weakest acid only to the anode. The preparation they used was mixed with proteoses. In the present research, the authors prepared their own pepsin from pig's stomach; they do not pretend it is absolutely pure, but at any rate it was free from any large admixture with grosser impurities. It always travelled to the anode; when, however, proteoses were added, it was carried more or less to the cathode also. No separation of pepsin from rennet occurred by this method. W. D. H.

The Influence of Hydrogen Ion Concentration on Trypsin Action. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, **36**, 280—290).—The principles of the experiments and the methods of interpreting the results are precisely the same as those used by the authors in their investigations on the influence of hydrogen ion concentration on the action of invertin (next page). They draw the conclusion that trypsin is an amphoteric electrolyte existing in solution in the form of anions, cations, or unchanged molecules according to the $[H^{\cdot}]$ concentration. Only the cations act proteoclastically, and the trypsin action is directly proportional to the number of these present in solution. The acid dissociation constant is 5.10^{-7}. Above 10^{-8} the tryptic action diminishes, possibly owing to the formation of doubly charged inactive anions. The optimal action takes place therefore in solutions when $[H^{\cdot}]$ concentration $=10^{-8}$.

S. B. S.

Preparation of Pure Invertase. REGINALD O. HERZOG (*Zeitsch. physiol. Chem.*, 1911, 74, 511. Compare Euler and Kullberg, this vol., i, 825).—Polemical. Euler and Kullberg have ignored the measurements of the molecular weight of invertase from the diffusion constants made by Herzog and Kasarnowski (Abstr., 1908, i, 707).

E. F. A.

The Action of Hydrogen Ions on Invertin [Invertase]. LEONOR MICHAELIS and HEINRICH DAVIDSOHN (*Biochem. Zeitsch.*, 1911, 35, 386—412).—The action of invertase on sucrose solutions was investigated in solutions with varying [H'] concentrations, and the zone of optimal action was found to occur between [H'] = $0{\cdot}65 \times 10^{-4}$ and $0{\cdot}98 \times 10^{-3}$. A standard curve was obtained when x, the amount of change (estimated polarimetrically), was plotted against t, the time of action of the ferment, the curve being constructed from the various data obtained from certain closely agreeing experiments carried out under conditions of optimal ferment action. Another curve was constructed when the ratio T/t and log[H] were plotted against one another, T being the time necessary to produce a given change read from the standard curve, t being the actual time taken to produce that change in the concentration [H]. The form of the curve thus obtained is similar to that of the dissociation curve of weak acids obtained by Michaelis. The conclusions drawn from the result are, that invertase is an amphoteric electrolyte with acid dissociation constant = 2×10^{-7} and basic dissociation constant 10^{-12}. The inverting action on sucrose is due to the presence of undissociated electrolyte, its optimum action corresponding with its isoelectric point. As $k_a k_b$ is greater than k_w, there is a broad isoelectric zone. Neither the cations nor the anions can act as ferments, and the action of the hydrogen ions depends, therefore, entirely on the degree of dissociation of invertase. The latter is not readily adsorbed by kaolin. Preliminary experiments on emulsin show that this is adsorbed to a greater extent than invertase.

S. B. S.

Influence of Certain Acids on the Inversion of Sucrose by Sucrase [Invertase]. FREDERICK STOWARD (*Bio-Chem. J.*, 1911, 6, 131—140).—Acids favour the inversion of sucrose by invertase. The action proceeds most rapidly when small amounts of sulphuric, hydrochloric, nitric, and phosphoric acid are present, and also in the presence of larger amounts of acetic acid. Increase of acid beyond a certain concentration, which differs in the case of different acids, retards, and finally arrests, the action.

W. D. H.

Diastase. JÓSEF BURACZEWSKI, L. KRAUZE, and A. KRZEMECKI (*Bull. Acad. Sci. Cracow*, 1911, [*A*], 6, 369—370).—Pure commercial diastase was treated in suspension in methyl alcohol with bromine or iodine. The compounds obtained contained 6·23% Br and 9·0% I respectively. When heated with water for half an hour, a greyish-white, insoluble substance, probably a halogenated protein, remained. The soluble portion was precipitated by alcohol, and behaved as a carbohydrate, giving a blue coloration with iodine like starch. Unchanged diastase converted it first into dextrin and then into reducing sugar;

mineral acids acted similarly. The carbohydrate gave the orcinol reaction. The phenylosazone obtained from the reducing sugar had m. p. 156—157°.

Diastase which has been boiled with very dilute mineral acids gives a blue coloration with iodine. It is regarded as an unstable compound of protein and a carbohydrate of the nature of starch, which is probably a pentosan. The araban described by Wroblewski as accompanying diastase is probably a dextrin-like decomposition product of this pentosan. E. F. A.

Action of Emulsin on Gentiopicrin in Alcohol. ÉMILE BOURQUELOT and MARC BRIDEL (*J. Pharm. Chim.*, 1911, [vii], 4, 385—390).—It has generally been assumed that the activity of emulsin is inhibited by small quantities of alcohol (compare Bougarel, *Thèse*, Paris, 1877), but the authors find that emulsin still hydrolyses gentiopicrin to a slight extent even in presence of 95° alcohol.

In alcohol at 60°, gentiopicrin is hydrolysed to the extent of 77·2% in forty days, and the action then stops. In 80° alcohol the same equilibrium is reached in seventy-five days, whilst in 85° alcohol 69·1% is hydrolysed in the same time. In 90° alcohol action ceases at the end of fifty-three days, when 48·4% of the glucoside is decomposed, and in 95° alcohol no further hydrolysis takes place after the twentieth day, when 6 to 7% of the glucoside is hydrolysed.

Even after keeping ninety days in alcohol of 80° strength, emulsin is still active towards gentiopicrin, although its activity is diminished by this treatment.

Emulsin is insoluble in alcohol over 50° in strength, but with progressive dilution of the alcohol with water it becomes more soluble, and saturated, filtered limpid solutions of the enzyme in 10° or 20° alcohol are almost as active as similar solutions in water. In alcohols of strength above 50°, emulsin appears therefore to act by simple contact. T. A. H.

The Ricinus Lipase. Y. W. JALANDER (*Biochem. Zeitsch.*, 1911, 36, 435—476).—The microscopic appearance of the mixture of fat and lipase in the presence of acetic acid and water vapour is described. The lipase imbibes water, and an emulsion is formed of the colloidal hydrated particles in oil (disperse phase). Details are given as to the methods for producing the oil–enzyme–acetic acid emulsion so as to obtain the maximum enzymatic activity. With 5 mg. enzyme (prepared by a modification of Nicloux's method) and 1 gram of triolein or cotton-seed oil, the best results are produced with about 0·6 c.c. of acetic acid. The concentration of the latter can vary between $N/500$ and $N/10$ without producing appreciable variations in the results. Much depends, however, on the mechanical treatment of the mixture, about which point full experimental details are given. The ricinus powder contains a small amount of acid which can be washed away. This washed powder in the presence of water alone is only slightly active. If it is first treated, however, with $N/10$-acid, it reaches its maximal activity in the presence of water alone. The results seem to indicate that a free acid plays the activating part in the enzyme action. By keeping the purified enzyme, however, for

some time with water or acid, its activity is diminished. The purified enzyme loses its activity when kept with neutral fats alone, without the presence of either acid or water. Of the fats investigated, triolein exerts the greatest action in this respect. In experiments lasting over one hour, the Schütz law $x/\sqrt{\epsilon}$ = constant (when x = amount saponified, ϵ = quantity of enzyme) was found to hold good over a comparatively large range. With more rapid hydrolysis, however, the law no longer held. The relationship between the time of action and the amount saponified was also investigated in numerous experiments. It was found that the relationship can be best expressed by the equation x/t^m = constant, when m varied between 0·57 and 0·70. No perfectly satisfactory formula could, however, be found. The lipase can also produce fats synthetically from oleic acid and glycerol. The presence of a small quantity of water, sufficient to produce the swelling of the lipase, accelerates the synthetical reaction, especially if the mixture be kept in continual rotation. S. B. S.

Synthesis of Fats by the Action of Enzymes. F. L. Dunlap and L. O. Gilbert (*J. Amer. Chem. Soc.*, 1911, **33**, 1787—1791).—Experiments are described which show that the lipase of castor oil seed is capable of effecting the synthesis of fat by its action on a mixture of glycerol and oleic acid (compare Taylor, *Univ. California Pub., Path.*, 1904, 1, 33, and Welter, this vol., i, 409). E. G.

Extraction of Zymase from Fresh Brewers' Yeast by Plasmolysis. P. Rinckleben (*Chem. Zeit.*, 1911, **35**, 1149—1150).—Brewers' yeast was incubated with glycerol (25 c.c. to 400 grams yeast) at 25° for fifteen to forty hours, whereby the yeast was plasmolysed and the mass became liquid. By filtering through hardened filter-paper, a liquid was obtained which, as a rule, was without fermentative activity. In a few cases, however, the liquid readily fermented sugars, whilst in others it was only active after the addition of a boiled yeast-juice. The last cases thus owed their inactivity to a disappearance of the co-enzyme of alcoholic fermentation during the plasmolysis.

An active liquid was also obtained when yeast was plasmolysed by means of disodium hydrogen phosphate in the presence of boiled yeast-juice which had previously been dried in a vacuum. W. J. Y.

p-Aminophenylarsine Tetraiodide. Aldo Patta and Piero Caccia (*Boll. Soc. Med.-Chirurg. Pavia*, 1911; Reprint, 9 pp. Compare Mameli and Patta, Abstr., 1909, i, 543; 1910, i, 531; also Bertheim, this vol., i, 593).—*p-Aminophenylarsine tetraiodide hydriodide*, $AsI_4 \cdot C_6H_4 \cdot NH_2,HI$, is obtained when *p*-aminophenylarsinic acid is heated with hydriodic acid (D 1·7) until iodine vapour is evolved in moderation; it forms orange-red crystals, m. p. 140°, and give a white, insoluble substance on treatment with water. The toxicity of this tetraiodide does not differ greatly from that of the atoxyl derivatives of Mameli and Patta (*loc. cit.*), but its injection produces a marked local action. R. V. S.

Preparation of Arsenophenols. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235430. Compare Abstr., 1909, i, 347; 1910, i, 453).—The reduction of hydroxyarylarsinic acids has been previously described, and the preparation of halogenated derivatives is now recorded. When sodium *p*-hydroxyphenylarsinite is treated with sodium hypochlorite (or hypobromite) in aqueous solution at the ordinary temperature, and the solution acidified after twelve hours, the dihalogenated acid (accompanied by trihalogenated phenol) separates; it crystallises from water, and does not melt below 260°.

p-Di-iodohydroxyphenylarsinic acid is obtained when sodium *p*-hydroxyphenylarsinite (285 parts) is treated with potassium iodate (110 parts) in dilute sulphuric acid solution, heated at 100°, and potassium iodide (220 parts) subsequently added; on cooling the product separates in crystalline form.

Tetrachloroarsenophenol, a yellow powder insoluble in water, is prepared by treating the foregoing dichloro-acid with alkaline sodium hyposulphite in the presence of magnesium chloride at 50° for some time; the corresponding *tetrabromo-* and *tetraiodo-arsenophenols* can be analogously prepared, have similar properties, and are decomposed at 200° into arsenophenol.

F. M. G. M.

Preparation of Aminohydroxyarylarsenious Oxides. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235391. Compare Abstr., 1909, i, 148).—*Aminohydroxyphenylarsenious oxide* separates as a colourless, microcrystalline powder when a very dilute sulphuric acid solution of aminophenolarsinic acid (Abstr., 1909, i, 804) is treated with potassium iodide, saturated with sulphur dioxide at the ordinary temperature, and subsequently rendered alkaline with ammonium hydroxide; it is somewhat soluble in water, readily so in mineral acids and alkali hydroxides.

F. M. G. M.

Nitro- and Amino-arsanilic Acids. ALFRED BERTHEIM (*Ber.*, 1911, 44, 3092—3098).—The toxicity of phenylarsinic acid is considerably diminished by the entrance of an amino-group into the benzene nucleus. A similar effect accompanies the introduction of a second amino-group, the toxicity of 3 : 4-diaminophenylarsinic acid being only one-twentieth that of *p*-aminophenylarsinic acid.

p-Oxalylaminophenylarsinic acid (D.R.-P. 231969),

$$CO_2H\cdot CO\cdot NH\cdot C_6H_4\cdot AsO(OH)_2,H_2O,$$

prepared by heating *p*-aminophenylarsinic acid or its sodium salt with oxalic acid, forms a white crystalline powder, consisting of short, microscopic prisms, which do not melt or decompose below 300°. On nitration, it yields 3-nitro-*p*-oxalylaminophenylarsinic acid, which forms almost colourless, short prisms, and is hydrolysed to 3-nitro-*p*-aminophenylarsinic acid, $NO_2\cdot C_6H_3(NH_2)\cdot AsO(OH)_2$. This crystallises in yellow needles, decomposing explosively above 300°; it is reduced by aqueous sodium hyposulphite to *3 : 4-diaminophenylarsinic acid*, $C_6H_3(NH_2)_2\cdot AsO(OH)_2,\frac{1}{2}H_2O$, which forms small, colourless prisms, m. p. 158—159° (decomp.), with previous darkening at 140°.

Aziminophenylarsinic acid, $N\!\left\langle{N-}\atop{NH}\right\rangle\!C_6H_3\cdot AsO(OH)_2$, prepared by

the action of nitrous acid on diaminophenylarsinic acid, crystallises in stout, colourless prisms, decomposing explosively above 300°.

The diamino-acid reacts with carbonyl chloride, yielding *o-phenylenecarbamidearsinic (benziminazolonearsinic) acid*,

$$CO{<}{}^{NH}_{NH}{>}C_6H_3\cdot AsO(OH)_2,$$

which crystallises in prisms or platelets, and with phenanthraquinone in glacial acetic acid solution to form *diphenylenequinoxalinearsinic (phenanthraphenazinearsinic) acid*, $\begin{matrix}C_6H_4\cdot C{:}N\\ |\\ C_6H_4\cdot C{:}N\end{matrix}{>}C_6H_3\cdot AsO(OH)_2$; both substances remain unchanged below 300°. F. B.

Preparation of Nitrohydroxyarylarsinic Acids. FARBWERKE VORM. MEISTER, LUCIUS & BRÜNING (D.R.-P. 235141).—When nitro-1-aminophenyl-4-arsinic acid (this vol., i, 594, 760) is stirred into a solution of potassium hydroxide (36 Bé) and heated at 80°, it yields the corresponding nitrophenol-4-arsinic acid, which is isolated by acidification, whilst by an analogous series of operations o-toluidine-4-arsinic acid furnishes nitro-*o*-cresol-4-arsinic acid. F. M. G. M.

Diphenylstibine Compounds. AUGUST MICHAELIS and ARWED GÜNTHER (*Ber.*, 1911, **44**, 2316—2320).—The substance produced by the reaction of triphenylstibine with antimony trichloride in presence of xylene is not chlorophenylstibine, as stated by Hasenbäumer (Abstr., 1899, i, 209), but chlorodiphenylstibine, $SbPh_2Cl$, and certain of the derivatives obtained from it have been described previously by Michaelis and Reese (Abstr., 1886, 885).

Chlorodiphenylstibine, m. p. 68°, crystallises from ether on addition of light petroleum, decomposes when heated in air, but melts unchanged under water, and irritates the skin when applied to it. Sodium carbonate converts it into *diphenylstibine oxide*, $O(SbPh_2)_2$, m. p. 78°, which separates on evaporation of its solutions in alcohol as an oil, which slowly solidifies into colourless needles. Both these substances have faint odours in the cold, but develop strong, unpleasant odours when heated. The oxide is transformed into *diphenylstibine sulphide*, m. p. 69°, by hydrogen sulphide in alcohol; it crystallises from hot alcohol in long, colourless needles. T. A. H.

Preparation of Nuclear Substituted Mercury Derivatives of Halogenated or Nitrated Phenols, or Halogenated Nitrophenols. FARBENFABRIKEN VORM. FRIEDR. BAYER & CO. (D.R.-P. 234851).—When halogen or nitro-derivatives of phenols are treated with mercuric oxide or mercuric salts, substitution products possessing both acidic and basic characters are formed; they can be purified by solution in alkali hydroxide and precipitation by carbon dioxide, and are decomposed by concentrated mineral acids into their generators.

p-Chlorophenylmercuric oxide was prepared by boiling *p*-chlorophenol with an aqueous acidified (sulphuric acid) solution of mercuric sulphate; *o-nitrophenylmercuric oxide*, a yellow powder, was prepared in an analogous manner, whilst *4-chloro-2-nitrophenylmercuric oxide*, a yellow, crystalline powder, was obtained from mercuric oxide and 4-chloro-2-nitrophenol in boiling acetic acid solution. F. M. G. M.

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.

2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.

3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.

4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.

5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.

6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.

7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.

8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.

9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulæ*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3\cdot CH_2\cdot CH_2\cdot CH_2I$ α-iodobutane, $CH_3\cdot CH_2\cdot CH_2\cdot CN$ α-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$\begin{matrix}CH_3\\CH_3\cdot CH_2\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CH_3\end{matrix} \quad \text{or} \quad CH_3\cdot CH_2\cdot CHMe\cdot CHMe\cdot CH_3$$

should be termed $\beta\gamma$-dimethylpentane not methylethyl*iso*propylmethane, and $\begin{matrix}CH_3\\CH_3\end{matrix}\!>\!CH\cdot CH\!<\!\begin{matrix}CH_3\\CO_2H\end{matrix}$ or $CH_3\cdot CHMe\cdot CHMe\cdot CO_2H$ should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3\cdot[CH_2]_5\cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

tives in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt{\cdot}CHMe{\cdot}CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3{\cdot}CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc{\cdot}CHMe{\cdot}CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2{\cdot}CO_2H$, and not $C_6H_3(OEt)_2{\cdot}CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, β-anilino-acrylic acid, $NHPh{\cdot}CH{:}CH{\cdot}CO_2H$, α-iminopropionic acid, $NH{:}CMe{\cdot}CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 3rd decade (1893–1902) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulæ the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulæ should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2 \cdot CH_2 \cdot CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO \cdot CH_3$, and Bz for $CO \cdot C_6H_5$.

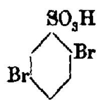
(c) That formulæ should be written *in one line* whenever this can be done without obscuring their meaning.

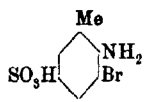
28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

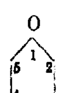
(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

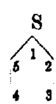
(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—

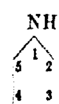

is 2 : 5-dibromobenzenesulphonic acid ;


is 3-bromo-*o*-toluidine-5-sulphonic acid.

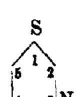
29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulæ should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical :—


Furan.


Thiophen.


Pyrrole.

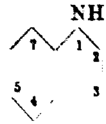

Oxazole.


Thiazole.


Pyrazole.

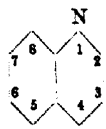
Purine.*

Pyridine.

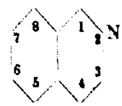


Indole.

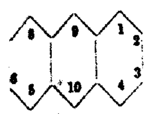
Naphthalene.



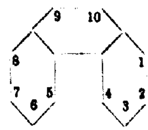
Quinoline.



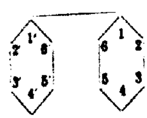
*iso*Quinoline.



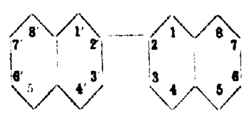
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying zes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be stened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the op left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, nd to check all formulæ and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor ot later than 24 hours after receipt from the printers.

***** The Editor's decision, in all matters connected with the bstracts, must be considered final.**

* This numbering, proposed originally by E. Fischer, is adopted in the text of the [illegible]

JOURNALS FROM WHICH ABSTRACTS ARE MADE

All references to Journals should give the abbreviated title, the year of publication, the series, the volume and the page; thus *Ber.* 1901, 34, 2455; *Bull. Soc. chim.* 1901, [iii], 25, 794; *Gazzetta* 1901, 31, i, 554.

Abbreviated Title.	Journal.
Amer. Chem. J.	American Chemical Journal.
Amer. J. Pharm.	American Journal of Pharmacy.
Amer. J. Physiol.	American Journal of Physiology.
Amer. J. Sci.	American Journal of Science.
Anal. Fis. Quim.	Anales de la Sociedad Española Fisica y Quimica.
Analyst	The Analyst.
Annalen	Justus Liebig's Annalen der Chemie.
Ann. Chim. anal.	Annales de Chimie analytique appliquée à l'Industrie, à l'Agriculture, à la Pharmacie et à la Biologie.
Ann. Chim. Phys.	Annales de Chimie et de Physique.
Ann. Falsif.	Annales des Falsifications.
Ann. Inst. Pasteur	Annales de l'Institut Pasteur.
Ann. Physik	Annalen der Physik.
Ann. sci. Univ. Jassy	Annales scientifiques de l'Université de Jassy.
Arch. expt. Path. Pharm.	Archiv für experimentelle Pathologie und Pharmakologie.
Arch. Hygiene	Archiv für Hygiene.
Arch. Néerland.	Archives Néerlandaises des sciences exactes et naturelles.
Arch. Pharm.	Archiv der Pharmazie.
Arch. Sci. phys. nat.	Archives des Sciences physiques et naturelles.
Arkiv Kem. Min. Geol.	Arkiv för Kemi, Mineralogi och Geologi.
Atti R. Accad. Sci. Torino.	Atti della Reale Accademia delle Scienze di Torino.
Atti R. Accad. Lincei	Atti della Reale Accademia dei Lincei.
Ber.	Berichte der Deutschen chemischen Gesellschaft.
Ber. Deut. bot. Ges.	Berichte der Deutschen botanischen Gesellschaft.
Ber. Deut. pharm. Ges.	Berichte der Deutschen pharmazeutischen Gesellschaft.
Ber. Deut. physikal. Ges.	Berichte der Deutschen physikalischen Gesellschaft.
* *Bied. Zentr.*	Biedermann's Zentralblatt für Agrikulturchemie und rationellen Landwirtschafts-Betrieb.
Bio-Chem. J.	The Bio-Chemical Journal.
Biochem. Zeitsch.	Biochemische Zeitschrift.
Boll. chim. farm.	Bollettino chimico farmaceutico.
Bull. Acad. roy. Belg.	Académie royale de Belgique—Bulletin de la Classe des Sciences.
Bull. Acad. Sci. Cracow	Bulletin international de l'Académie des Sciences de Cracovie.
Bull. Acad. Sci., St. Pétersbourg.	Bulletin de l'Académie Impériale des Sciences de St. Pétersbourg.
Bull. Assoc. chim. Sucr. Dist.	Bulletin de l'Association des chimistes de Sucrerie et de Distillerie.
Bull. Geol. Soc. Amer.	Bulletin of the Geological Society of America.
Bull. Imp. Inst.	Bulletin of the Imperial Institute.
Bull. Soc. chim.	Bulletin de la Société chimique de France.
Bull. Soc. chim. Belg.	Bulletin de la Société chimique de Belgique.
Bull. Soc. franç. Min.	Bulletin de la Société française de Minéralogie.
Bull. Soc. ind. Mulhouse	Bulletin de la Société industrielle de Mulhouse.
Centr. Bakt. Par.	Centralblatt für Bakteriologie, Parasitenkunde und Infektionskrankheiten.
Centr. Min.	Centralblatt für Mineralogie, Geologie und Palaeontologie.
* *Chem. Zentr.*	Chemisches Zentralblatt.
Chem. News	Chemical News.
Chem. Rev. Fett-Harz-Ind.	Chemische Revue über die Fett- und Harz-Industrie.

* Abstracts from the *Zentralblatt* are made only in the case of papers published in journals other than those included in this list.

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

ABBREVIATED TITLE.	JOURNAL.
Chem. Weekblad	Chemisch Weekblad.
Chem. Zeit.	Chemiker Zeitung.
Compt. rend.	Comptes rendus hebdomadaires des Séances de l'Académie des Sciences.
Exp. Stat. Record	Experiment Station Record.
[illegible]	Gazzetta chimica italiana.
[illegible]	Geological Magazine.
[illegible]	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie.
[illegible] Min. Beil.-Bd.	Neues Jahrbuch für Mineralogie, Geologie und Palaeontologie. Beilage-Band.
Jahrb. Radioaktiv. Elektronik.	Jahrbuch der Radioaktivität und Elektronik.
J. Amer. Chem. Soc.	Journal of the American Chemical Society.
J. Biol. Chem.	Journal of Biological Chemistry, New York.
J. Chim. phys.	Journal de Chimie physique.
J. Geol.	Journal of Geology.
J. Hygiene.	Journal of Hygiene.
J. Ind. Eng. Chem.	Journal of Industrial and Engineering Chemistry.
J. Inst. Brewing	Journal of the Institute of Brewing.
J. Landw.	Journal für Landwirtschaft.
J. Med. Research	Journal of Medical Research.
J. Path. Bact.	Journal of Pathology and Bacteriology.
J. Pharm. Chim.	Journal de Pharmacie et de Chimie.
J. Physical Chem.	Journal of Physical Chemistry.
J. Physiol.	Journal of Physiology.
J. pr. Chem.	Journal für praktische Chemie.
J. Roy. Agric. Soc.	Journal of the Royal Agricultural Society.
J. Roy. Soc. New South Wales.	Journal of the Royal Society of New South Wales.
J. Russ. Phys. Chem. Soc.	Journal of the Physical and Chemical Society of Russia.
J. Soc. Chem. Ind.	Journal of the Society of Chemical Industry.
J. Soc. Dyers	Journal of the Society of Dyers and Colourists.
J. Washington Acad. Sci.	Journal of the Washington Academy of Sciences.
K. Svenska Vet.-Akad. Handl.	Kongl. Svenska Vetenskaps-Akademiens Handlingar.
Lancet.	The Lancet.
Landw. Versuchs-Stat.	Die landwirtschaftlichen Versuchs-Stationen.
Le Radium	Le Radium.
Mem. Accad. Sci. Torino	Memorie della Reale Accademia delle Scienze di Torino.
Mem. Coll. Sci. Eng. Kyōtō.	Memoirs of the College of Science and Engineering, Kyōtō Imperial University.
Mem. Manchester Phil. Soc.	Memoirs and Proceedings of the Manchester Literary and Philosophical Society.
Metallurgie	Metallurgie.
Milch. Zentr.	Milchwirtschaftliches Zentralblatt.
Min. Mag.	Mineralogical Magazine and Journal of the Mineralogical Society.
Monatsh.	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
Nuovo Cim.	Il Nuovo Cimento.
Pflüger's Archiv.	Archiv für die gesammte Physiologie des Menschen und der Thiere.
Pharm. J.	Pharmaceutical Journal.
Pharm. Weekblad	Pharmaceutisch Weekblad.
Pharm. Zeit.	Pharmazeutische Zeitung.
Pharm. Zentr.-h.	Pharmazeutische Zentralhalle.
Philippine J. Sci.	Philippine Journal of Science.
Phil. Mag.	Philosophical Magazine (The London, Edinburgh and Dublin).

JOURNALS FROM WHICH ABSTRACTS ARE MADE.

Abbreviated Title.	Journal.
Phil. Trans.	Philosophical Transactions of the Royal Society of London.
Physikal. Zeitsch.	Physikalische Zeitschrift.
Proc. Amer. Physiol. Soc.	Proceedings of the American Physiological Society.
Proc. Camb. Phil. Soc.	Proceedings of the Cambridge Philosophical Society.
Proc. K. Akad. Wetensch. Amsterdam.	Koninklijke Akademie van Wetenschappen te Amsterdam. Proceedings (English version).
Proc. Phil. Soc. Glasgow	Proceedings of the Glasgow Philosophical Society.
Proc. Physiol. Soc.	Proceedings of the Physiological Society.
Proc. Roy. Soc.	Proceedings of the Royal Society.
Proc. Roy. Soc. Edin.	Proceedings of the Royal Society of Edinburgh.
Quart. J. exp. Physiol.	Quarterly Journal of experimental Physiology.
Quart. J. Geol. Soc.	Quarterly Journal of the Geological Society.
Rec. trav. chim.	Recueil des travaux chimiques des Pays-Bas et de la Belgique.
Rend. Accad. Sci. Fis. Mat. Napoli.	Rendiconto dell' Accademia delle Scienze Fisiche e Matematiche-Napoli.
Rev. de Métallurgie	Revue de Métallurgie.
Sci. Proc. Roy. Dubl. Soc.	Scientific Proceedings of the Royal Dublin Society.
Sci. Trans. Roy. Dubl. Soc.	Scientific Transactions of the Royal Dublin Society.
Sitzungsber. K. Akad. Wiss. Berlin.	Sitzungsberichte der Königlich Preussischen Akademie der Wissenschaften zu Berlin.
Sitzungsber. K. Akad. München.	Sitzungsberichte der königlich bayerischen Akademie der Wissenschaften zu München.
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society.
Trans. Faraday Soc.	Transactions of the Faraday Society.
Trans. Nova Scotia Inst. Sci.	Transactions of the Nova Scotia Institute of Science.
Trans. Path. Soc.	Transactions of the Pathological Society.
Trans. Roy. Soc. Canada	Transactions of the Royal Society of Canada.
Trans. Roy. Soc. Edin.	Transactions of the Royal Society of Edinburgh.
Trans. Roy. Irish Acad.	Transactions of the Royal Irish Academy.
Tsch. Min. Mitt.	Tschermak's Mineralogische Mitteilungen.
U.S.A. Dept. Agric. Bull.	Bulletins of the Department of Agriculture, U.S.A.
U.S.A. Dept. Agric. Rep.	Reports of the Department of Agriculture, U.S.A.
Verh. Ges. deut. Naturforsch. Aerzte	Verhandlung der Gesellschaft deutscher Naturforscher und Aerzte.
Wiss. Abhandl. Phys.-Tech. Reichsanstalt.	Wissenschaftliche Abhandlungen der Physikalisch-Technischen Reichsanstalt.
Zeitsch. anal. Chem.	Zeitschrift für analytische Chemie.
Zeitsch. angew. Chem.	Zeitschrift für angewandte Chemie.
Zeitsch. anorg. Chem.	Zeitschrift für anorganische Chemie.
Zeitsch. Biol.	Zeitschrift für Biologie.
Zeitsch. Chem. Ind. Kolloide.	Zeitschrift für Chemie und Industrie der Kolloide.
Zeitsch. Elektrochem.	Zeitschrift für Elektrochemie.
Zeitsch. Kryst. Min.	Zeitschrift für Krystallographie und Mineralogie.
Zeitsch. Nahr. Genussm.	Zeitschrift für Untersuchung der Nahrungs- und Genussmittel.
Zeitsch. öffentl. Chem.	Zeitschrift für öffentliche Chemie.
Zeitsch. physikal. Chem.	Zeitschrift für physikalische Chemie, Stöchiometrie und Verwandtschaftslehre.
Zeitsch. physiol. Chem.	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
Zeitsch. prakt. Geol.	Zeitschrift für praktische Geologie.
Zeitsch. Ver. deut. Zuckerind.	Zeitschrift des Vereins der deutschen Zucker-Industrie.
Zeitsch. wiss. Photochem.	Zeitschrift für wissenschaftliche Photographie, Photophysik und Photochemie.
Zeitsch Zuckerind. Böhm.	Zeitschrift für Zuckerindustrie in Böhmen.

General and Physical Chemistry.

The Density and Refraction of the System Furfuraldehyde + Water. F. Schwers (*Bull. Acad. roy. Belg.*, 1911, 641—652).—The densities and refractive indices of binary mixtures containing 4·6, 5·7, 6·5, and 96·3% of furfuraldehyde have been measured at different temperatures.

Curves are plotted to show the volume contraction which occurs in the formation of the various solutions in its dependence on the temperature. These curves exhibit certain irregularities, which in the case of the dilute furfuraldehyde solutions are similar to those which have been observed previously in the case of mixtures of water with diacetyl glycol and ethyl acetoacetate.

In regard to the refractive index, the observed values differ from those calculated by an amount which is more or less independent of the composition and the temperature of the binary mixture. Observations with the hydrogen lines H_a and H_β and the yellow helium line show that the difference depends on the wave-length of the light used. H. M. D.

Refractive Indices of Liquid Crystals. Paul Gaubert (*Compt. rend.*, 1911, **153**, 573—576. Compare Abstr., 1909, ii, 529; Wallerant, *ibid*).—The author records observations on the refractive indices of the isotropic forms of cholesterol, cholesteryl benzoate, acetate, decoate, and propionate; also of mixtures of the latter with the decoate and with *p*-azoxyphenetole. Measurements could not be made in the case of some of the mixtures, owing to solidification of the superfused liquid taking place without production of the optically positive anisotropic phase.

The difference between the refractive index of the isotropic liquid and the liquid crystal is small. Crystals of the doubly refractive liquid phase, produced before solidification, are optically positive, whilst those belonging to the anisotropic liquid phase existing at a higher temperature are negative. The experiments on mixtures showed that their optical properties do not follow the laws relating to the mixture of isomorphous solid crystals, apparently owing to the occurrence of one substance in a polymorphous, crystalline liquid form, unknown in the pure substance. W. O. W.

The Secondary Spectrum of Hydrogen. C. Porlezza (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 176—183).—The measurements of the secondary spectrum of hydrogen have now been extended to the yellow and red regions, as far as λ 6963, and to the ultra-violet as far as λ 3295. New lines are found in both regions, as well as in the region λ 4807—4253. The wave-lengths are tabulated. Certain lines observed by Croze (this vol., ii, 558) are not found, and the differences are possibly due to the difference in diameter of the capillaries used by the two observers, otherwise the lines found only by Croze must

be due to the presence of an impurity (compare Watson, Abstr., [illegible], ii, 453). C. H. D.

The Ratio of the Intensities of the Series Lines of Hydrogen in the Canal Ray Spectrum. FRITZ LUNKENHEIMER (*Ann. Physik*, 1911, [iv], 36, 134—152).—The relative intensities of the lines H_α and H_β in the hydrogen canal ray spectrum have been measured for different velocities of the luminous particles. For this purpose the intensities of the two lines were compared with that of light of the same wave-length emitted by a Nernst lamp, and also by a Geissler discharge tube, which were operated under constant conditions. In some experiments, the comparison was effected subjectively, and in others by means of photographic records. Within the limits of the errors of experiment, the results obtained show that the ratio of the intensities of the two hydrogen lines is independent of the velocities of the canal ray particles. This is opposed to the results obtained by Stark and Steubing (Abstr., 1908, ii, 546), who found that an increase in the velocity of the particles is accompanied by an increase in the relative intensity of the lines of smaller wave-length. It is probable that the relative intensities are dependent on the gas pressure in the discharge tube, and this may account for the divergent results obtained by Stark and Steubing. H. M. D.

The Resonance Spectra of Iodine Vapour and their Destruction by Gases of the Helium Group. ROBERT W. WOOD (*Phil. Mag.*, 1911, [vi], 22, 469—481. Compare this vol., ii, 169, 170).—A method is described by which the resonance spectra of iodine can be exhibited to an audience by means of a Cooper-Hewitt lamp and a small pocket spectroscope. With the improved illumination of the vapour which can be obtained by means of suitably arranged quartz-mercury arc lamps and a cylindrical vapour tube, new photographs of the resonance spectra excited by the green and the two yellow mercury lines have been obtained. The spectrum excited by the green line consists of a series of equidistant lines, eighteen members of which are shown in the photographic records. The two yellow lines give rise to a series of fifteen equidistant doublets, two of which are situated below and twelve above the exciting lines. The series excited by $\lambda = 5790 \cdot 5$ is much more intense than the series due to $\lambda = 5769 \cdot 5$; this is probably due to a closer coincidence between the wave-length of the less refrangible yellow line of mercury and one of the absorption lines of the iodine vapour. The wave-lengths of the various lines are considered to be correct to about one Ångstrom unit. From a comparison of the wave-length differences in each series, it is found that these increase as the red end of the spectrum is approached.

As the result of a comparison of the effects produced by the various inert gases in transforming the resonance spectrum into the banded spectrum, which is excited by white light, it is found that helium is the most active. In presence of krypton at 1·7 mm. pressure, the band spectrum could only just be distinguished, and with xenon at 1·5 mm. pressure, no trace of the band spectrum was found, although the

intensity of the resonance emission was reduced to about one-fourth of its original value.

Farther observations in which the vapour was excited by polarised light show that the resonance lines are themselves polarised, and from this it may be inferred that the directed motion passed over by the light waves to the resonant electron is passed on as directed motion to the other electrons. When in presence of helium the resonance spectrum is completely replaced by the band spectrum; the emitted light is still found to be partially polarised. H. M. D.

The Colorimetric Dilution Law. ARTHUR HANTZSCH (*Annalen*, 1911, **384**, 135—142. Compare Piccard, this vol., ii, 561).—Piccard's views are at variance with the results of the author's experiments on chromoisomerides, which show that Beer's law is untenable even for isomerides. The law holds for the structurally unchangeable ethyl diethylacetoacetate and ethyl ethoxycrotonate in all solvents, but in the case of ethyl acetoacetate in hexane the equilibrium is shifted with increasing dilution in the direction of the more strongly absorptive enol form, a result which is confirmed in a purely chemical way by titration with bromine (Meyer, this vol., i, 350, 832, 833).

The author also shows that Beer's law is inapplicable to solutions of the colourless and the yellow modifications of ethyl dichlorodihydroxyterephthalate and of the colourless and the yellow forms of *o*-nitroaceto-*p*-toluidide (all of which are unimolecular in solution), and also to the chromoisomeric pyridine, quinoline, and acridine salts (this vol., i, 673).

Contrary, therefore, to Piccard's views, the author is of opinion that the untenability of Beer's law denotes the existence of chromoisomerides in equilibrium in the solution, provided that polymerides have previously been shown to be absent. C. S.

The Colour of Iodine Solutions. HEINRICH LEY and K. VON ENGELHARDT (*Zeitsch. anorg. Chem.*, 1911, **72**, 55—62).—A re-examination of the absorption spectrum of freshly prepared solutions of iodine in ethyl alcohol confirms the results formerly obtained (Abstr., 1910, ii, 813) with a single band at $1/\lambda$ 2150. The different results obtained by Waentig (Abstr., 1910, ii, 117) and Crymble, Stewart, and Wright (*ibid.*, 470), showing two absorption bands, are due to the use of old solutions. The gradual decomposition may be followed spectroscopically.

The violet solutions of iodine in hexane or chloroform have identical spectra, with a band at $1/\lambda$ 2000 and another in the ultra-violet. Beer's law is not followed, especially in the ultra-violet region. The ethereal solution is intermediate in character, and the differences between the spectra are less than those found by Waentig. The absorption coefficients of a solution of iodine in benzene show that in this case, also, the head of the band lies at $1/\lambda$ 2000. It is held that the brown solutions contain additive compounds, I_2L_m, but the constitution of the violet solutions is still uncertain. C. H. D.

Absorption Spectra of Triphenylmethyl and of Salts of Triphenylcarbinol. KURT H. MEYER and HEINRICH WIELAND (*Ber.*, 1911, **44**, 2557—2559).—Non-conducting solutions of triphenylmethyl (and also of other triarylmethyls) in organic solvents are sharply distinguished from the triphenylmethyl ion, assumed to be present in solutions of salts of triphenylcarbinol, by means of the spectroscope. Whilst the latter exhibit continuous absorption in the more refrangible region of the (visible) spectrum, solutions of triphenylmethyl are characterised by a banded spectrum consisting of one strong, sharply defined band and a second, which is weaker.

The conducting solution of triphenylmethyl in liquid sulphur dioxide exhibits the continuous absorption of the triphenylmethyl ion (probably, therefore, a salt-like additive compound of solute and solvent is formed), but after removing the sulphur dioxide by a current of carbon dioxide and dissolving the residue in benzene, the yellow solution shows the banded spectrum of triphenylmethyl. These results are claimed to be in harmony with Baeyer's theory (Abstr., 1905, i, 281). C. S.

Crystalline Liquids. H. VON WARTENBERG (*Physikal. Zeitsch.*, 1911, **12**, 837—839. Compare Bose, 1909, ii, 383; this vol., ii, 184). —The optical behaviour of the crystalline liquid forms of *p*-azoxyanisole and *p*-azoxyphenetole has been examined when the turbid liquids are subjected to the influence of a magnetic field. Observations were made with parallel and convergent polarised rays of light and in directions parallel and at right angles to the lines of force. Both substances were found to behave like uniaxial crystals, and thus the crucial test suggested by Nernst (*Zeitsch. Elektrochem.*, 1910, **16**, 702) is in favour of Bose's theory of the liquid crystalline state of aggregation. The magnetic field has no influence on the clearing temperature in either of the substances investigated.

H. M. D.

Development of Colours on Fibres by Light Energy. OSKAR BAUDISCH (*Chem. Zeit.*, 1911, **35**, 1141—1142).—Silk and wool may be dyed a brilliant cherry-red, which is quite fast, by treating the fabric with an aqueous ammoniacal solution of the ammonium salt of α-nitrosonaphthylhydroxylamine, steaming, drying, and finally exposing to the action of light.

During the steaming process, the α-nitrosonaphthylhydroxylamine, which is fixed on the fibres, decomposes with the formation of α-nitrosonaphthalene; the latter substance, probably aided by the reducing action of the animal fibre, then changes into α-azoxynaphthalene, which under the influence of light becomes red, in all probability owing to its transformation into the corresponding hydroxyazonaphthalene.

It is not improbable that other nitrosoarylhydroxylamines will be found to behave in a similar manner.

α-*Nitrosonaphthylhydroxylamine* is a white, crystalline substance, which is very sensitive to the action of light; the *ammonium* salt crystallises in white leaflets, and is most readily obtained by the

ation of amyl nitrite on a cold solution of α-nitronaphthylhydroxylamine containing an excess of ammonia; the *copper* salt,

$$(C_{10}H_7O_2N_3)_2Cu,$$

crystallises from chloroform in glistening, greyish-blue needles; the iron salt is very soluble in ether, forming an intense red solution.

W. H. G.

The Ranges of α-Particles from Various Radioactive Substances and a Relation between the Range and Period of Transformation. HANS GEIGER and J. M. NUTTALL (*Phil. Mag.*, 1911, [vi], 22, 613—621).—A film of the active substance was placed centrally in a silvered globe of 8 cm. radius, and the ionisation current in air determined at various pressures. This is independent of the pressure until the range of the α-particle becomes equal to the radius of the globe. At this point the ionisation current begins to diminish as the pressure is further reduced. From the point of inflexion on the curve the range is found, and from this the initial velocity of the α-particle can be calculated. The results obtained are given in the table:

Substance.	Range at 15°.	Range at 0°.	Initial velocity.
Uranium	2·72 cm.	2·58	1·51 × 10⁹ cm./sec.
Ionium	3·00 ,,	2·84	1·56 ,,
Radium	3·30 ,,	3·13	1·61 ,,
Polonium	3·77 ,,	3·58	1·68 ,,
Thorium	2·72 ,,	2·58	1·51 ,,
Radio-thorium ...	3·87 ,,	3·67	1·70 ,,

If the logarithm of the range is plotted against the logarithm of the period of transformation, the points for the uranium-radium series fall approximately on a straight line, whilst those for the actinium series fall on another straight line of similar slope, parallel to the first. The thorium series is still being investigated. The results in the other two series include in each case five α-ray-giving products. The period of ionium calculated from the range of its α-particles is nearly one million years. That of radium-*C* similarly calculated should be about a millionth of a second. The range is proportional to the cube of the velocity, so that similar straight lines would result on plotting the logarithm of the periods and of the velocity of the α-particles. On this rule, which at present is empirical, an explanation suggests itself why no α-rays of low range are known, for the period of transformation would be so great that the activity would be beyond the limit of detection.

F. S.

Production of Helium by Radium. BERTRAM B. BOLTWOOD and ERNEST RUTHERFORD (*Phil. Mag.*, 1911, [vi], 22, 586—604).—A quantity of radium chloride, freed from radio-lead and polonium by treatment with hydrogen sulphide after addition of bismuth, lead, and antimony, was sealed up in a Jena glass combustion tube and the air exhausted. By γ-ray measurements the quantity of radium was found to be 0·191 gram. Re-measured at the close of the experiments the quantity found was 0·193 gram. In the first experiment the time of accumulation was eighty-three days, and the volume of helium

evolved on heating the tube was 6·58 cu. mm. at *N.T.P.* In the second experiment the time of accumulation was 132 days, and, after the withdrawal of the gases, the radium chloride was dissolved in dilute hydrochloric acid and the helium collected. The total helium was 10·38 cu. mm. The two results agree in giving the rate of production of helium per gram of radium, in equilibrium with its first three α-ray-giving products, as 156 cu. mm. per year. The theoretical rate, calculated from the number of α-particles expelled, is 158 cu. mm. The radium standard employed was 97·22% pure in terms of that used in the atomic weight determinations by Thorpe. The production of helium from a known amount of radium emanation was found to be in fair agreement with that calculated. The production of helium was also observed from preparations containing polonium.

F. S.

The Relative Number of Ions Produced by the β-Particles from the Various Radioactive Substances. HANS GEIGER and ALOIS F. KOVARIK (*Phil. Mag.*, 1911, [vi], 22, 604—613).—By assuming that the ionisation produced by a β-particle does not depend appreciably on the velocity, and examining cases where the β-ray-giving product is in equilibrium with an α-ray-giving product, the relative number of ions produced per atom disintegrating by the β-rays can be determined; for the number of α-particles can be counted, and this is identical with the number of atoms breaking up giving β-rays. The ionisation due to β-rays divided by this number gives the β-ray ionisation per atom disintegrating. The number of α-particles was determined by an ionisation method at low pressure from data previously accumulated (Abstr., 1909, ii, 473), and checked by scintillation experiments. The number of ions produced per cm. of path per atom disintegrating was found to be similar in the case of the β-ray products thorium-*D* and the corresponding actinium product, and about twice as great as in the cases of radium-*E* and uranium-*X*, whilst radium-*C* was intermediate. In the first case the number found was 136, in the second 69 and 78, and in the third 108. The most probable explanation is that different numbers of β-particles are expelled per atom disintegrating in the different cases. If it is assumed that two β-particles are given per atom of thorium-*D*, the number of ions produced per cm. in air by a high velocity β-particle is 67. This is higher than Durack's value, in which, however, the reflexion of the β-particles by the walls of the ionisation chamber was not corrected for.

F. S.

The Emission of Electrons in Chemical Reactions. FRITZ HABER and GERHARD JUST (*Ann. Physik*, 1911, [iv], 308—340. Compare Abstr., 1909, ii, 853; this vol., ii, 572).—An improved method is described for the investigation of the electron emission which takes place when electro-positive metals react with certain gases. With this apparatus experiments have been made in which a potassium sodium alloy was allowed to react with the vapour of carbonyl chloride at very low pressure, the surface of the reacting alloy being continuously renewed by the formation of a rapid succession of drops at

the extremity of a silver capillary terminating in the neighbourhood of a silver plate connected with the electric discharge measuring apparatus.

The results of these experiments confirm previous conclusions, and show that the reaction at the ordinary temperature and in the absence of light is accompanied by the emission of electrons, resulting in the charging of the alloy to a potential of about one volt. That the carriers of the electric discharge are free electrons is proved by the behaviour towards a magnetic field.

When the carbonyl chloride is replaced by bromine, free electrons are also emitted, but if the sodium–potassium alloy is replaced by sodium-, potassium-, or lithium-amalgam, negative ions are produced. In all cases the effect is of unipolar character, and is observed in the entire absence of light. H. M. D.

Transformation and Nomenclature of the Radioactive Emanations. ERNEST RUTHERFORD and HANS GEIGER (*Phil. Mag.*, 1911, [vi], 22, 621—629).—The new short-lived products of transformation of the thorium and actinium emanations give α-rays, and have half-value periods respectively of 0·14 sec. and 0·002 sec. (compare next abstract). In each case they carry positive charges when produced, and are carried in an electric field to the negative electrode, constituting, therefore, the first members of the active deposits analogous to radium-*A* (compare Geiger, this vol., ii, 683). They may be put into evidence in the dark by immersing a rod coated with zinc sulphide into the emanations. On charging it negatively, the end instantly lights up, and as suddenly dies out when the rod is discharged. The actinium product of period 0·002 sec. was observed by Giesel eight years ago (Abstr., 1903, ii, 193) in this phenomenon, which he termed the "*E*-rays." The thorium product can be put into evidence by driving an endless wire, by a motor, through small holes in ebonite corks closing a cylinder containing a source of thorium emanation, and charging the wire negatively. The wire, as it leaves the cylinder, is active when the motor is working, and its activity and the decay along the wire can be examined by a zinc sulphide screen. It is proposed to call the new products thorium-*A* and actinium-*A*, in accordance with the nomenclature in the radium series, where radium-*A*, the first short-lived α-ray-giving product of the emanation, has been known from the start. Hence the next rayless products, previously termed thorium-*A* and actinium-*A*, will now be designated thorium-*B* and actinium-*B*, and are thus made analogous to the rayless product radium-*B*. The next two α-ray-giving products of thorium are termed thorium-C_1 and -C_2, analogously to radium-C_1 and -C_2, the β-ray succeeding product is termed thorium-*D* as at present, the corresponding actinium products being also termed actinium-*C* and actinium-*D*. The group radium-C_1 and -C_2 corresponds with the *C* and *D* members of their series, in that radium-C_2, and possibly radium-C_1, also gives β- and γ-rays. On the new nomenclature, the *A* substances are short-lived, and give α-rays; the *B* substances are the longest lived of the active deposit products, and give only feeble non-penetrating β-rays. The *C* substances all give α-rays, and in the case of radium,

β and γ-rays also, the D substances of thorium and actinium giving the β- and γ-rays. F. S.

Radioactive Products of Short Life. H. G. J. MOSELEY and KASIMIR FAJANS (*Phil. Mag.*, 1911, [vi], **22**, 629—638).—A source of actinium or thorium emanation was contained in an ebonite box, open at one end, the edges of which, covered with velvet pressed against a disk capable of rotation at a high speed. Inside the box was a metal gauze which could be positively charged with respect to the disk, so causing the short-lived products actinium-A and thorium-A (compare preceding abstract) to be deposited on the rotating disk. Two sector-shaped ionisation chambers, the faces of which opposite the disk were covered with gold-beater's skin and aluminium leaf, were arranged in definite positions on the periphery of the disk, and the ionisation in them compared with the disk revolving at known speed. From the decay of activity over the period required for the disk to turn from opposite the first to opposite the second ionisation chamber, the periods of the products were determined. The half-period of actinium-A was found to be 0·002 second, λ being 347 (sec.$^{-1}$), and that of thorium-A 0·145 second. With similar apparatus an examination was made of the active deposit of actinium to test the question whether the α-ray-producing member actinium-C was complex (compare Abstr., 1910, ii, 768). No evidence of any short-lived product was found, the formation of the β- and γ-ray producing actinium-D appearing to follow the disintegration of actinium-C directly. F. S.

The Number of Ions Produced by the β- and γ-Rays from Radium-C. A. S. EVE (*Phil. Mag.*, 1911, [vi], **22**, 551—562).—By the use of very lightly built electroscopes of known capacity, constructed out of light metal rods covered with thin aluminium foil, the number of ions produced by the β- and γ-rays respectively of known quantities of radium at known distances from the electroscope has been determined. For the γ-rays, the radium preparation was surrounded with thin cylinders of zinc or lead, and placed between the poles of an electromagnet to deflect the β-rays. The β-rays were used from various sources, the most satisfactory being from a thin leaf of aluminium coated with the active deposit. The total number of ions produced per second by the γ-rays from a curie of radium-C (the radium-C, in equilibrium with 1 gram of radium) is $1{\cdot}1 \times 10^{15}$, the number produced per c.c. per second at a distance of 1 cm. from the radium-C, in air at atmospheric pressure, is $3{\cdot}74 \times 10^9$. Corresponding values for the β-rays are 4×10^{14} and $1{\cdot}3 \times 10^{11}$, but these could only be approximately evaluated. The average number of ions made by the flight of one β-particle of radium-C is $1{\cdot}2 \times 10^4$, or about 48 ions per cm. of path, assuming that one curie produces $3{\cdot}4 \times 10^{10}$ β-particles per second. It is estimated that only one out of every 180 molecules traversed by the β-particle is ionised. If the γ-ray is considered as an entity, one being expelled per atom of radium-C disintegrating, it produces 3×10^4 ions on the average, or 1·2 ions per cm. of path. Calculating from the ionisations as a measure of the

energy, the heating effects of radium, 110 calories per gram per hour, are due, 103·5 calories to α-rays, 2·0 to β-rays, and 4·5 to γ-rays.

F. S.

The Concentration and Isolation of Radioactive Substances by "Fractional Adsorption." ERICH EBLER and M. FELLNER (*Ber.*, 1911, **44**, 2332—2338 *).—The method employed is to shake the solution for some hours with metasilicic acid gel, (prepared by the hydrolysis of dilute vapour of silicon tetrachloride and subsequent dialysis; this vol., ii, 723), and then to volatilise the silicic acid by means of hydrofluoric acid. With dilute solutions of radium barium chloride, from 90 to 100% of the radium was so adsorbed and concentrated in a preparation from one-fourth to one-fiftieth of the initial weight in different experiments. With radio-lead 86 to 95% was adsorbed, and the concentration of weight was from one-third to one hundredth, but the separate activities of the constituents, radium-*D*, -*E* and -*F*, are not stated. The radium-*F* was adsorbed more than the radium-*D*. With uranium-*X*, the greater part of the active matter was adsorbed. Many advantages are claimed for the method. The small quantities of the materials adsorbed are of no disadvantage. Greater concentration of the material by a single operation is possible than by any other process, and no intermediate products result as in ordinary fractional crystallisation. F. S.

Valency in Gaseous Ionisation. J. FRANCK and W. WESTPHAL (*Phil. Mag.*, 1911, [vi], **22**, 547—551).—The conclusion of Millikan and Fletcher (this vol., ii, 573) that ionisation of gases by radium or Röntgen rays is never accompanied by the liberation of more than one electron from a gas molecule, is considered to be irreconcilable with certain observations. Although the conditions necessary for the production of multivalent ions have not yet been established, there can be little doubt that such ions are formed in certain circumstances. H. M. D.

The Carriers of Electricity in Gases. A. BECKER (*Ann. Physik*, 1911, [iv], **36**, 209—280).—The author has investigated the nature of the carriers of the electric charge in gases ionised by Röntgen rays, ultra-violet light, and cathode rays.

Under the influence of Röntgen rays, dust-free gases give rise solely to rapidly moving carriers, and the presence of water or other vapours appears to have no influence on the mobility of the carriers. This behaviour differs from that found in the ionisation of gases by ultra-violet light, the much larger, slowly moving carriers which are formed in this case being probably due to chemical changes brought about by the ultra-violet rays. The condensation nuclei which give rise to the large carriers do not appear to be the immediate consequence of this action, for evidence has been obtained in favour of the view that these nuclei result from the action of the product of the chemical change on traces of foreign vapours present in the gas.

In the case of gases which contain oxygen, the primary product is probably ozone, and this, by interaction with substances like sulphur

* and *Zeitsch. anorg. Chem.*, 1911, **73**, 1—30.

dioxide, ammonia, and hydrogen sulphide, gives rise to solid or liquid particles. The activity of ozone in the formation of slowly moving carriers has been examined in detail, and found to depend on the concentration both of the ozone and of the vapour with which the ozone reacts.

Cathode rays give rise to a much smaller number of the slowly moving carriers, and it is supposed that these are not really due to the cathode rays, but to the action of the ultra-violet light which accompanies the cathode ray radiation.

In reference to the rapidly moving carriers, experiments are described which show that these are of larger dimensions than the gas molecules. Whatever the nature of the condensation process which is involved in the production of these carriers, it appears that the process takes place very rapidly, and may be considered complete after the lapse of a few tenths of a second. In this respect the condensation process differs from that resulting in the formation of the slowly moving carriers. H. M. D.

Ionisation of Gases by Canal Rays. R. SEELIGER (*Physikal Zeitsch.*, 1911, **12**, 839—842).—Canal rays from a discharge tube were made to pass between the plates of a condenser arranged so as to measure the ionisation produced, and the rays were then collected by means of a cylindrical receiver which enabled the number of positively charged particles to be determined.

In hydrogen, at a pressure of 0·01 mm., the relationship between the saturation ionisation current and the positive charge acquired by the receiver indicates that n particles give rise to $n/3$ ions per cm. In oxygen the number of ions produced is about four times as large. For small variations of pressure the number of ions generated is proportional to the gas pressure, but is independent of the velocity of the canal rays as measured by the magnitude of the discharge potential. H. M. D.

Radioactive Ions. J. FRANCK and LISE MEITNER (*Ber. Deut. physikal. Ges.*, 1911, **13**, 671—675).—To test Wellisch's hypothesis, that ions in a mixture of gases retain their charge for only a short time and can pass it on from one kind of molecule to another, the mobility found experimentally being a mean of the mobilities of different charged molecules, experiments have been made with the positively charged recoil atoms of thorium-D expelled from the active deposit of thorium. Two brass tubes connected to the poles of a battery were fitted concentrically into a glass tube. The opposed ends of the brass tubes were covered with wire gauze; the one of which connected to the negative pole was made active in the thorium emanation before the experiment. A current of air or hydrogen was maintained through the tubes from the positive inactive to the negative active gauze, the recoiled atoms of thorium-D thus having to travel with the field against this gas stream. The mobility of the recoiled atoms could thus be deduced from the velocity of gas stream necessary to prevent the atoms reaching the negative gauze. The mobility in air was between 0·7 and 1·6 cm./sec. for unit $P.G.$, and in

hydrogen greater than 5 cm./sec. These values are, within the error of experiment, the same as apply for other ions in these gases. This result is opposed to Wellisch's hypothesis, for the method would remove from the gas the recoiled atoms when they lost their charge, with the result that much smaller mobilities would be shown by these gases than has been found. F. S.

The Spontaneous Charging of Polonium. NORMAN CAMPBELL (*Physikal. Zeitsch.*, 1911, 12, 870—871).—Hauser's views (this vol., ii, 685) relating to the part played by δ-rays in the spontaneous charging of a polonium plate are criticised. The assumption that the number of rays which leave the active plate when at a potential of *V* is equal to the number which have a kinetic energy greater than *eV* is unjustifiable. The data obtained in the investigation of the penetrating power of the rays permit also of an alternative explanation. According to this the primary δ-rays are completely absorbed by extremely thin layers, and the changes which are observed on increasing the thickness of these layers are due to the absorption of α-rays and the production of secondary δ-rays. H. M. D.

Application of the Content of Uranium and Lead of Some Minerals to the Determination of the Ages of the Rocks containing Them. FERRUCCIO ZAMBONINI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 131—138).—The author criticises the work of Strutt (Abstr., 1910, ii, 1023) and of Holmes (this vol., ii, 570) on the determination of the age of rocks by means of the ratio between the amounts of lead and uranium contained in them. The mean values deduced by Holmes for rocks of the Christiania district of Norway can have little significance, because the differences between the values calculated for different rocks (admittedly of the same formation) are very great; in fact, the calculated age of that deposit varies from 336 to 558 million years. The author has collected analytical data, due to Blomstrand and others, for a number of other minerals of the same formation, and from them deduces ages varying from 41 million years to 17,302 million years. Notably discordant results (935 to 1533 million years) are also obtained when different specimens of the same mineral (uraninite) from the formation in question are considered. The Norwegian formation is not exceptional, for similar irregularities are observed in the results from the deposits of gadolinite in Texas (mentioned by Boltwood) and for thorianite from Ceylon. Among the reasons for the inapplicability of this method for estimating geological time, the following are adduced: (1) Strutt's formula, if it is to lead to exact results, demands more precise determination of the ratio Pb/U than is possible at present; (2) most of the minerals hitherto examined have suffered far-reaching change since they first came into existence; (3) the method requires that the lead contained in the mineral shall have originated solely from the uranium; in that case the ratio Pb/U for minerals of the same formation should be constant, whereas Holmes found (in the case of the Christiania formation) that the ratio usually increases as the percentage of uranium diminishes. R. V. S.

The Intensity of the Earth's Penetrating Radiation at Different Altitudes and a Secondary Radiation Excited by It. J. C. McLENNAN and E. N. MACALLUM (*Phil. Mag.*, 1911, [vi], 22, 639—646).—The intensity of the earth's penetrating radiation was compared, in a hermetically sealed zinc vessel of 30 litres capacity and 0·5 mm. wall-thickness, at different heights. On the ground at Toronto, 5·8 more ions per c.c. per second were produced than on the ice on Toronto Bay, and this was assumed to be the measure of the penetrating radiation. On a clock tower of the City Hall, 64 metres high, the difference was 2·8 ions per c.c. per second, so that at this height the rays are diminished to 48 per cent. This is in agreement with Eve's calculation (this vol., ii, 89). A secondary radiation due to the earth's penetrating radiation was observed from a high brick wall encircling the university lawn. It extended a distance of 14 or 15 metres, and thus corresponds with β-rays. This produces about 1·5 ions per c.c. per second. F. S.

Radioactivity of Certain Russian Mineral Springs. P. G. MEZERNITZKY (*J. Russ. Phys. Chem. Soc.*, 1911, 43, *Phys. Part*, 244—255).—The author has examined electrometrically a number of mineral waters from various parts of Russia, all of which exhibit radioactivity, some of them to a greater degree than the waters of Carlsbad, Marienbad, Nauheim, Gastein, etc. T. H. P.

Conductivities, Temperature-coefficients of Conductivity and Dissociation of Certain Electrolytes. H. H. HOSFORD and HARRY C. JONES (*Amer. Chem. J.*, 1911, 46, 240—278. Compare Abstr., 1910, ii, 256).—The electrical conductivity of aqueous solutions of some fifteen inorganic salts has been measured at temperatures between 0° and 65° and at dilutions ranging from 2 to 4096 litres per mol. The salts examined include a number of alums and other double salts.

In agreement with previous results, it is found that the temperature-coefficients are generally much greater for the salts which form hydrated salts at the ordinary temperature than for those which separate out in the anhydrous form. In addition to the dehydration of hydrates, decrease in polymerisation is a probable cause of abnormally rapid increase in conductivity with rise of temperature, and there is evidence that sulphates are polymerised in concentrated solutions.

The data for solutions of the violet and green varieties of potassium and ammonium chromium sulphates show that the change from the violet to the green modification is accompanied by an increase in conductivity, the magnitude of which becomes smaller as the solutions become more dilute, and may become negative. This is attributed to the greater resistance of the green modification to the hydrolytic action of the solvent. Previous measurements at 25° have shown that the conductivities of double salts are less than the sum of the conductivities of the constituent salts. The same relationship holds at all temperatures from 0° to 65°, and the conductivity data show further that the dissociation of such double salts is but slightly affected by change of temperature. H. M. D.

Conductivity, Temperature-coefficients of Conductivity, and Dissociation of Certain Electrolytes in Aqueous Solution from 0° to 35°. Probable Inductive Action in Solution and Evidence for the Complexity of the Ion. L. G. WINSTON and HARRY C. JONES (*Amer. Chem. J.*, 1911, **46**, 368—413).—In continuation of earlier work (Jones and Hosford, preceding and earlier abstracts), determinations have been made, at temperatures from 0° to 35° and at various dilutions, of the electrical conductivity and dissociation of the following thirty salts: ammonium nitrate and sulphate, ammonium hydrogen sulphate, sodium sulphate, borax, potassium acetate and permanganate, dipotassium hydrogen phosphate, strontium acetate, magnesium bromide, nitrate, formate and acetate, cadmium chloride, bromide and iodide, lead chloride, aluminium chloride, nitrate and sulphate, chromium chloride and sulphate, manganous sulphate, silver nitrate, cobalt bromide, copper sulphate, uranyl chloride, nitrate, sulphate and acetate.

In general, the results obtained confirm those of the earlier experiments. It has been found that, in all cases, the conductivity increases with rise of temperature and with dilution. The temperature-coefficients, expressed in conductivity units, increase with rise of temperature, except in the case of ammonium hydrogen sulphate and uranyl sulphate, whilst when expressed as percentages they decrease in all cases. The more highly hydrated salts have large temperature-coefficients, and, from a consideration of these constants, the amount of hydration seems to be closely related to the water of crystallisation.

At certain dilutions, cadmium iodide, chromium chloride, uranyl acetate, and silver nitrate show an increase in percentage dissociation as the temperature rises. Cadmium iodide and lead chloride, which have no water of crystallisation, have temperature-coefficients as large as those of highly hydrated salts, such as copper sulphate. These instances appear to be exceptions to the results obtained previously, and indicate that there must be some other factor operating which produces the same effect as hydration. It is considered probable that, in such cases, inductive action takes place through the solvent between charged ions and neutral molecules, and that this gives rise to the formation of complex molecules and ions in solution. E. G.

The Dielectric Constant of Certain Liquids at High Pressures. RUDOLF ORTVAY (*Ann. Physik*, 1911, [iv], **36**, 1—24).—The influence of pressure on the dielectric constant of ethyl ether, benzene, toluene, xylene, carbon disulphide, chloroform, paraffin, light petroleum, and castor oil has been measured for pressures up to 500 atmospheres. Nernst's method, in the differential form described by Philip, was employed in the measurements. In all cases, the dielectric constant increases with the pressure in such a way that it can be accurately represented by an equation of the form $Dp = D_1(1 + \alpha p + \beta p^2)$, in which α is positive and β negative. $\alpha \cdot 10^4$ varies from 2·187 for ethyl ether to 0·538 for paraffin, and $\beta \cdot 10^7$ from 0·714 for ethyl ether to 0·324 for paraffin.

In the case of benzene, toluene, and xylene, the variation of the dielectric constant with the pressure is nearly the same.

The value of $(D-1)v/(D+2)$, in which v represents the [illegible] volume of the liquid, was found to diminish to the extent of 1·3% [illegible] ethyl ether and of 1·17% for benzene, when the pressure is raised from 1 to 500 atmospheres. H. M. D.

Chemico-physical Investigations on Animal Liquids. IV. Technique of the Electrometric Method for the Study of the Reaction of the Liquids of the Organism. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 107—111. Compare Abstr., 1908, ii, 869).—In the practical application of the electrometric method to the study of the reaction of organic liquids, an important difficulty is due to the diffusion potential which is set up between the liquid under examination and the standard liquid. The author has compared the results obtained by the two methods of overcoming this difficulty in use, namely, (1) the addition of an excess of a neutral electrolyte to both solutions; (2) the insertion of a concentrated solution of potassium chloride between the two liquids (compare Bjerrum, Abstr., 1905, ii, 793). His concentration cells were as follows respectively: H | serum | KCl(1·75 or 3·5N) | HCl(0·01N) | H and H | serum | NaCl (0·125N) | HCl (0·01N) + NaCl (0·125N) | H. The results show a small difference of electromotive force amounting to about 0·0025 volt, that of the former cell being the greater. Reasons are adduced in favour of the second method being the more correct. R. V. S.

Normal Elements. P. J. H. VAN GINNEKEN and HUGO R. KRUYT (*Zeitsch. physikal. Chem.*, 1911, 77, 744—760).—A theoretical paper. In the first section the requirements of a satisfactory normal element are considered. The second section is mainly an extension of the views of Reinders (compare Abstr., 1902, ii, 639) on the application of the phase rule to a normal element, regarded as a system [illegible] in equilibrium. The general condition for a normal element is that it must be composed of two parts, both of which are in themselves invariant systems (as regards temperature and pressure) of the same components. G. S.

Transport Numbers and Molecular Complexity. ARRIGO MAZZUCCHELLI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 124—12[illegible]).—The author has worked out equations, based on Einstein's formula (compare Lorenz, Abstr., 1910, ii, 577), connecting transport numbers and molecular complexity, and proposes to employ them to determine the degree of polymerisation of certain electrolytes. R. V. S.

A Case of Electrolytic Saturation Current. GEORGE JAFFÉ (*Ann. Physik*, 1911, [iv], 36, 25—48).—Measurements of the electric conductivity of solutions of lead oleate in hexane and light petroleum indicate that saturation currents can be obtained similar to those observed in the ionisation of gases. The conductivity apparatus consisted of a condenser with guard-ring and parallel electrodes, the distance between which could be varied. The applied potential differences were varied from 500 to 3000 volts per cm., and [illegible]

current measured by means of a Curie piezo-quartz apparatus with a Dolezalek electrometer as null instrument. For potentials (e) greater than about 500 volts per cm. the current (i) can be represented by the equation $i = a + ce$, in which a and c are constants. Since a is relatively very large, it follows that the current is mainly carried by ions which are formed at such a slow rate that a condition of saturation is attained. The residual current (ce) is probably due to impurities which it is impossible to avoid entirely.

It is shown that the rates of formation and of re-combination of the ions of the lead oleate can be deduced from the experimental observations. Both processes are of the second order, and the degree of ionisation is therefore independent of the concentration of the salt. From experiments on the influence of temperature on the conductivity, it is found that the temperature-coefficient of the rate of formation of the ions is negative between 0° and room temperature, and then becomes positive as the temperature rises further.

Some observations relating to the conductivity of solutions of ethyl alcohol in light petroleum are also recorded. Under ordinary conditions, such solutions exhibit unipolarity, a negative temperature-coefficient, and an abnormally rapid increase of the current with increasing potential. This is found to be due to traces of impurities, for when carefully purified materials are employed, the anomalous phenomena disappear. H. M. D.

Magneto-optical Effects Exhibited by Chlorine and Iodine.

A. Heurung (*Ann. Physik*, 1911, [iv], **36**, 153—176).—Two forms of apparatus are described by means of which the author has investigated the influence of a magnetic field on the optical behaviour of chlorine and iodine, both of which give a banded absorption spectrum. In the case of chlorine the rotation of the plane of polarisation was measured for wave-lengths varying from $\lambda = 518\mu\mu$ to $\lambda = 640\mu\mu$, but the data show no appreciable increase in rotation in the region of absorption. The behaviour of an absorption band towards a magnetic field appears therefore to be quite different from that of individual absorption lines.

From observations with iodine vapour between crossed nicols, it has been found that the application of a magnetic field gives rise to considerable illumination in the green part of the spectrum, and several new lines make their appearance. This magneto-optical effect could not be eliminated by rotation of the analysor or by the insertion of a quarter-wave plate, from which it appears that only a small portion of the light is polarised. The effect of the magnetic field on the individual absorption lines obtained by using a grating was also examined, but no change could be detected. Between crossed nicols, some of these lines become brighter when the field is applied, but the resulting light emission is not polarised to more than a small extent. H. M. D.

Adjustable Electric Signal Thermometer.

Franz Michel (*Chem. Zeit.*, 1911, **35**, 1111).—An apparatus on the principle of Beckmann's thermometer, so arranged that electrical contact will be

made at any pre-arranged temperature and an audible or visible signal thereon given. L. DE K.

Specific Heat of Water. ANDRÉ COTTY (*Ann. Chim. Phys.*, 1911, [viii], **24**, 282—288).—Determinations of the specific heat of water in a Bunsen calorimeter, provided with a special device for measuring the temperature of the water added, show that the specific heat is 1·0067 at 0°, diminishes to 0·9994 at 20°, and then rises to 1·005 at 35°. The specific heat at 15° is taken as unity. These figures agree closely with those of Bartoli and Stracciati (Abstr., 1893, ii, 443; 1895, ii, 5, 6). T. A. H.

Measurements of Specific Heat at Low Temperatures with the Copper Calorimeter. F. KOREF (*Ann. Physik*, 1911, [iv], **36**, 49—73).—The copper calorimeter described by Nernst and Lindemann (Abstr., 1910, ii, 263) has been employed for the measurement of the mean specific heats of a large number of substances over the temperature intervals $-190°$ to $-80°$ and $-80°$ to 0°. It is shown that accurate results can be obtained by the author's method of operating, which is described in detail.

Data are recorded for aluminium, copper, zinc, lithium, sodium, potassium, boron, graphite, diamond, bromine, the halogen salts of sodium and potassium, calcium fluoride, oxide, hydroxide and carbonate, silver iodide, lead iodide, quartz and carbon disulphide. In addition, the latent heat of vaporisation of carbon disulphide was measured, the mean value obtained being 86·87 cals. The experimental data are finally discussed from the point of view of Nernst's heat theorem, and also in relation to the Planck-Einstein theory of energy quanta. H. M. D.

The Energy Content of Solid Substances. WALTHER NERNST (*Ann. Physik*, 1911, [iv], **36**, 395—439).—The chief results of the work described in this paper have been published previously (compare Abstr., 1910, ii, 263; this vol., ii, 368, 464, 466). The substances for which the energy content can be calculated with the aid of a single frequency number include both elements and compounds, the latter being such that the vibration frequencies of the component atoms are nearly equal. For other elements, such as sulphur and carbon (as graphite), and compounds like silica (quartz), lead chloride, silver chloride, mercurous chloride, silver iodide, and benzene, the use of two or more frequency numbers is necessary. These frequencies have been calculated in a number of cases, and from these the values of the energy content are derived and compared with the experimental values.

From the observed convergence of the atomic heats of solid crystalline and amorphous substances towards zero at very low temperatures, it follows that the conception of temperature ceases to have any meaning in respect of all those properties which are dependent on the average behaviour of the atoms. Such properties are, for example, energy content, volume, compressibility, and chemical potential, and since chemical potential is a measure of free energy, it appears that the author's heat theorem must be regarded as a special case of a more general principle.

On the basis of the knowledge furnished by this investigation of the variation of the energy content with the temperature, the way has been paved for the development of a theory of the solid state of aggregation which should allow of the deduction of the most important properties of solids in a simple manner. H. M. D.

Prevention of Bumping. H. SPURRIER (*J. Amer. Chem. Soc.*, 1911, **33**, 1632—1633).—It is sometimes necessary, especially in soap and oil analyses, to remove alcohol from an aqueous solution which is covered with a layer of oil. In boiling such a liquid great inconvenience is caused by bumping. This difficulty can be overcome by introducing a piece of glass tube, open at both ends, into the vessel, one end of the tube being below, and the other above, the surface of the liquid. If a beaker is used, it should be covered whilst ebullition is proceeding, in order to prevent loss by the spurting of small quantities of the liquid up the tube. E. G.

A Simple Direct Electrical Method of Determining Heats of Vaporisation. NICOLAI N. NAGORNOFF and L. ROTINJANZ (*Zeitsch. physikal. Chem.*, 1911, **77**, 700—706).—The comparison method with electrical heating described by Marshall and Ramsay (compare Abstr., 1896, ii, 349) is employed. The arrangement used is described and figured, and the mode of working described in detail. The external glass mantle, a cylindrical vessel 6 cm. wide and 17 cm. long, is sealed on to a Liebig's condenser and is well insulated. The boiling vessel, a glass beaker 4 cm. wide and 11 cm. high, is filled with the liquid to be vaporised, and rests on narrow supports on the base of the outer vessel, which is closed by a well-ground stopper through which the wires conveying the current pass. For further details the original paper must be consulted.

It is shown that the results are in good agreement with those obtained by previous observers by the electrical method, but are rather higher than those obtained by the calorimetric method. The cause of this discrepancy has not been elucidated.

The heats of vaporisation of certain compounds, in calories per gram, are as follows: *cyclo*Hexane, 85·4; methyl*cyclo*hexane, 76·4; chloro*cyclo*hexane, 74·9; *cyclo*hexanol, 108·1; ethyl *n*-propyl ether, 82·7, and ethyl *iso*butyl ether, 74·9. The value of Trouton's constant for all the compounds examined is close to 21·0, except for *cyclo*hexanol, which, like other hydroxyl compounds, gives a much higher value (24·9). G. S.

Relation of Heat of Vaporisation to other Constants at the Boiling Temperature of Some Liquids at Atmospheric Pressure. JACK P. MONTGOMERY (*Amer. Chem. J.*, 1911, **46**, 298—307).—For a number of non-associated liquids which yield normal vapours, certain relationships are shown to exist at the ordinary boiling point. For such normal liquids the heat of vaporisation is proportional to the volume of unit weight of the saturated vapour; it is also proportional to the square of the velocity of the molecules. The quantity of heat required to vaporise unit volume of such a liquid is

proportional to the number of molecules in this volume and to the absolute temperature. In the case of isomeric substances the absolute boiling temperature is in many cases proportional to the density of the liquid at the boiling point. Finally, the absolute boiling temperature is directly proportional to the molecular weight and to the square root of the number of atoms in the molecule, and inversely proportional to the relative size of the molecules as measured by the quantity b in van der Waals' equation.

From a consideration of these relationships, the conclusion is drawn that none of the heat of vaporisation is required for intra-molecular work, but that all the heat is used up in overcoming cohesion and in giving the molecules sufficient kinetic energy to balance the pressure of the surrounding atmosphere. H. M. D.

Molecular Attraction and the Properties of Liquids. RICHARD D. KLEEMAN (*Phil. Mag.*, 1911, [vi], **22**, 566—586. Compare this vol., ii, 257).—A theoretical paper in which various forms of the equations connecting the internal heat of vaporisation and the surface tension of liquids with the temperature, density, and the density of the saturated vapour are further discussed. H. M. D.

[Variation of Vapour Pressure with Temperature.] IVAR W. CEDERBERG (*Zeitsch. physikal. Chem.*, 1911, **77**, 707—718).—On the basis of considerations partly theoretical and partly experimental, the vapour-pressure formula: $A \log^2 p + B \log p + C = \theta_0/T - 1$ is deduced, where θ_0 is the critical temperature on the absolute scale, and A, B, and C are constants to be determined from the experimental data. In the form $\log p = [A' - (B'\theta_0)/T]^{\frac{1}{2}} - C'$, where A', B', and C' are new constants, this formula has been tested through a wide range of temperature from $-10°$ upwards, and is found to represent the experimental results more satisfactorily than any other formula hitherto proposed. At very low temperatures, Nernst's well-known formula gives slightly better results. G. S.

Apparatus for Continuous Working in Fractional Distillations in a Vacuum. LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 30—35).—The apparatus carries two flasks as receivers, and is so constructed that either of them can be removed and replaced without altering the pressure inside the apparatus even momentarily, so that the distillation may be really continuous. R. V. S.

Heat of Combination of Acidic Oxides with Sodium Oxide. VII. WILLIAM G. MIXTER (*Amer. J. Sci.*, 1911, [iv], **32**, 202—206. Compare Abstr., 1910, ii, 585, 828).—The heat changes involved in the action of sodium peroxide on copper, silver and gold, and the corresponding oxides have been determined. The results show that the higher oxides of these metals combine with sodium oxide with considerable development of heat to form compounds which are stable at high temperatures. The following data are recorded: $CuO + O + Na_2O = Na_2O,CuO_2 + 29500$ cal.; $2Ag + 2Na_2O_2 =$

$Na_2O,Ag_2O_2 + Na_2O + 6000$ cal.; $2Ag + O_2 + Na_2O = Na_2O,Ag_2O_2 + 44000$ cal.; $Ag_2O + O + Na_2O = Na_2O,Ag_2O_2 + 39400$ cal.; $2Ag + O = Ag_2O + 5400$ cal.; $2Au + 3Na_2O_2 = 3Na_2O,Au_2O_3 + 30400$ cal.; $Au_2O_3 + 3Na_2O = 3Na_2O,Au_2O_3 + 100900$ cal.; $2Au + 3O = Au_2O_3 - 12300$ cal. H. M. D.

Thermochemical Studies. IV. Diazo- and Azo-compounds. WOJCIECH SVENTOSLAVSKY (*Ber.*, 1911, 44, 2429—2437.* Compare Abstr., 1910, ii, 588, 691).—The measurements already described (*loc. cit.*) have been repeated with improved methods, care being taken, in particular, to maintain the experimental room below 3°. The results are substantially as before, with the exception that the heat of neutralisation of benzenediazonium hydroxide is 11·68 cal. instead of 13·7 cal. The heats of neutralisation of *o*- and *p*-tolyldiazonium hydroxides are 12·06 cal. and 13 cal. respectively. The heat of formation of the normal diazo-salts when hydrolysis is almost completely absent is 6·85 cal. for diazobenzene and 5·34 cal. for *p*-diazotoluene. E. F. A.

Thermochemical Studies. V. Diazo- and Azo-compounds. Monoamines. WOJCIECH SVENTOSLAVSKY (*Ber.*, 1911, 44, 2437—2445.† Compare Abstr., 1910, ii, 588, 691).—The heats of diazotisation of a number of mono- and di-amines have been determined by the methods already described (*loc. cit.*). The heat of diazotisation of the NH_2 group varies slightly with the constitution of the amine; it depends on three factors, the heat of neutralisation of the diazonium compound, the true heat of diazotisation, and the heat of salt formation of the amine. The introduction of a methyl group in the ortho-position increases the magnitude of the first two factors. The heats of diazotisation of benzidine and dianisidine are less than those of aniline and *o*-toluidine; this is probably due to the influence of the adjoining phenyl radicles on the basic nature of the diazonium base. The heat of formation of the diazo-salt is greater for derivatives of benzidine and dianisidine than for diazobenzene and its homologues. The heat of combination of the diazo-compounds with β-naphthol is more nearly a constant, but a correction must be applied for the difference between the heat of neutralisation of the diazonium hydroxide and of sodium hydroxide. E. F. A.

Pyknometer for Density Determinations. LUDWIG VON KREYBIG (*Chem. Zeit.*, 1911, 35, 1120).—The determination of the density of viscous liquids is often accompanied by difficulties caused by the liquid adhering to the parts of the pyknometer above the mark, etc. The pyknometer devised by the author consists of a small flask fitted with a stop-cock in the lower part of the neck. The bore of the stop-cock is very wide, and there are two holes of the same width in the neck of the flask where the stopper fits. In making a density determination, the flask is filled with the viscous liquid, the stop-cock connecting with the body of the flask and the neck. When the temperature is constant, the stopper is turned through 90°, and any

* and *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1060—1075.
† and *J. Russ. Phys. Chem. Soc.*, 1911, 43, 1076—1083.

liquid in the neck and bore of the stopper is removed by means of a volatile solvent, after which the weighing can be made. The results are trustworthy to the fourth decimal place. T. S. P.

Volume Changes in the Formation of Solutions. HERMANN WOLFF (*Ann. Physik*, 1911, [iv], 36, 177—182).—From a consideration of the free energy changes, the author deduces a relationship between the differential volume effects which accompany the absorption of small quantities of water or alcohol by a given mixture of these two substances. Available data are insufficient to test the validity of the differential equation. H. M. D.

Viscosity and Fluidity of Suspensions of Finely-divided Solids in Liquids. EUGENE C. BINGHAM and T. C. DURHAM (*Amer. Chem. J.*, 1911, 46, 278—279. Compare this vol., ii, 372).—The viscosity of suspensions of infusorial earth, china clay, and graphite ("Aquadag") in water and ethyl alcohol has been measured at different temperatures by means of an Ostwald viscometer having a capillary of relatively large diameter and about 40 cm. long. The fluidity decreases rapidly as the proportion of the suspended solid increases, the decrease being directly proportional to the volume concentration of the solid. By extrapolation of the fluidity concentration curves it is found that the fluidity becomes zero at a definite concentration which is independent of the temperature and of the dimensions of the particular apparatus used in the viscosity determinations. The volume concentration corresponding with zero fluidity varies with the nature of the solid suspension, and when the same solid is suspended in different liquids the zero fluidity concentrations are not necessarily the same.

The fluidity of solid suspensions in water is altered considerably when small quantities of electrolytes are added, hydrogen and hydroxyl ions having a specially large influence.

Incidentally, attention is drawn to the considerable errors which frequently occur in the use of Ostwald viscometers as a consequence of the neglect to take into account the kinetic energy imparted to the liquid in its motion through the capillary. H. M. D.

The Viscosity of Binary Liquid Mixtures in the Neighbourhood of the Critical Dissolution Temperature. PAUL DRAPIER (*Bull. Acad. roy. Belg.*, 1911, 621—640).—Measurements of the viscosity of *cyclo*hexane, nitrobenzene, aniline and *n*-hexane, and of various mixtures of the first pair and the last pair of liquids have been made at a series of temperatures in the neighbourhood of the respective critical dissolution temperature.

In the case of the pure liquids, the fluidity diminishes with rise of temperature according to the equation $\phi = a + b(t - 20°)$. Mixtures exhibit a similar relationship at temperatures much higher than the critical dissolution temperature, but as this temperature is approached, the fluidity temperature curves show marked deviations and become concave to the temperature axis.

The fluidity of the two series of binary mixtures can be additively represented in terms of the fluidities of the components if the

temperature is sufficiently removed from the critical, but in the neighbourhood of this dissolution temperature the isothermal fluidity concentration curves deviate considerably from the requirements of the additive law. The observed variations in viscosity are supposed to be connected with certain changes in the liquid which give rise to the phenomenon of opalescence, and in this connexion reference is made to the possibility of explaining the viscosity relationships on the basis of the views of Donnan and of Smoluchowski. H. M. D.

Adsorption of Solutions. II. GERHARD C. SCHMIDT (*Zeitsch. physikal. Chem.*, 1911, **77**, 641—660).—In a previous paper (Abstr., 1910, ii, 1041) a formula was proposed which represents satisfactorily the adsorption by charcoal of acetic acid from aqueous solution through a considerable range of concentration. For still greater variations of concentration, however, the formula is not valid, nor does it express the fact that adsorption is an equilibrium phenomenon. Regarding the amount of adsorption as determined by equilibrium between the adsorbing force and the solution pressure, the formula $[(a-x)S]/v = Kxe^{A(S-x)/S}$ is deduced, in which x represents the amount adsorbed, a the amount of solute originally present, v the volume, S the maximum amount adsorbed, and A and K are constants. The formula represents the results satisfactorily when the concentration of the charcoal is varied in the ratio 1 : 8, and that of the acetic acid in the ratio 1 : 3000.

The objections raised by Marc (compare this vol., ii, 258) to the author's theory are not valid. In particular, there is no evidence of discontinuity in the adsorption curve of acetic acid by charcoal, as suggested by Marc. G. S.

Anomalous Adsorption. ALFRED LOTTERMOSER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 135—136).—The occurrence of maximum adsorption at a particular concentration, which was observed by Biltz (Abstr., 1910, ii, 830) in the adsorption of certain colouring matters, has also been found by the author in the adsorption of potassium iodide from aqueous solution by silver iodide. This anomalous behaviour is found to be due to an increase in the size of the silver iodide particles under the influence of the potassium iodide solution. The solvent action of the more dilute solutions and the precipitation which accompanies increase in concentration lead to the formation of a more dense and apparently crystalline modification from the originally amorphous silver iodide. H. M. D.

Diffusion of Electrolytes in Colloids. LUIGI ROLLA (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 47—51).—The author has worked out a method for determining the coefficient of diffusion, k^2, in Fourier's equation: $\partial c/\partial t = k^2.\partial^2 c/\partial t^2$ by measurement of the time elapsing before the maximum electromotive force is attained between two electrodes immersed in gelatin into which an electrolyte is allowed to diffuse. The arrangement employed consists of a glass tube containing two parallel, plane, circular, silver disks, which are perforated with many small holes. The tube is filled with pure gelatin in such a

manner that the surface of the gel at the bottom of the tube is plane and parallel to the electrodes. A solution of the electrolyte (potassium chloride, sodium chloride) is circulated past this gelatin surface for a short time; pure water is then substituted for the electrolyte (so that the concentration on the external surface of the gelatin is zero), and the time required for the electromotive force to reach a maximum is observed. The results agree well with those obtained by other methods. R. V. S.

Aggregation and Crystallisation of Water in Connexion with the Physical Condition of Substances. I. SAWORNOFF (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 107—112).—Observations relating to the formation and liquefaction of ice crystals are described which lead the author to the conclusion that liquid water must be regarded as having a definite molecular structure ("latent crystalline structure") and not as a chaotic aggregation of molecules, as is usually assumed. In reference to this view, the physical properties of water in the different states of aggregation are examined in some detail. H. M. D.

Isomerism and Polymorphism. HANS STOBBE (*Ber.*, 1911, 44, 2732—2735).—The author's views (Abstr., 1910, i, 623) having been misunderstood by Biilmann (this vol., i, 367), the former discusses them again.

Where in two substances having the same empirical composition, the atoms are differently arranged in dissimilar molecules, the substances are isomeric chemical compounds, but where identical molecules are differently grouped in dissimilar crystals, the substances are two forms of presentation (Erscheinungsformen), two species (Gattungen) or modifications of a single polymorphous chemical compound. Where the two substances are isomerides, their differences are present, not only in the crystalline form, but also in the dissolved and fused states. With the two modifications of a single chemical compound, however, the two solutions are identical, as also are the two fused masses. On these assumptions, the limits between isomerism and polymorphism are sharply drawn, and there is no limiting region, such as Biilmann imagines from the author's previous considerations.

To determine which of these two cases exists in a particular instance often presents considerable practical difficulties, especially when the two individuals either have closely approximating physical constants or show a high velocity of transformation. The author regards calcspar and aragonite as two modifications of dimorphous calcium carbonate; rutile, anatase, and brookite as three modifications of trimorphous titanium oxide, and the four crystallographically different monochloroacetic acids as modifications of a single tetramorphous acid, and so on; and, in general, he regards such chemical compounds as polymorphous so long as there is no certain proof of the existence of two chemically different calcium carbonates, etc. He regards it as beyond doubt, however, that improved methods will in some cases result in compounds at present looked on as modifications

of "one" dimorphous chemical substance being considered later as "two" truly isomeric compounds (compare Schaum, Abstr., 1910, i, 391). T. H. P.

Colloidal Chemistry of Histological Silver Staining. RAPHAEL E. LIESEGANG (*Koll. Chem. Beihefte*, 1911, 3, 1—46).—Cajal's method of staining nerve tissue by means of a silver solution has been examined from the colloido-chemical point of view, and the conditions are formulated which must be observed in order to ensure satisfactory preparations. A comparison is made between the various phases of the staining process and those involved in the development, toning, and fixing of a photographic plate. H. M. D.

The Significance of the Degree of Dispersity in the Investigation of the General Properties of Sulphur Hydrosols. SVEN ODÉN (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 100—106).—Methods of preparing sulphur hydrosols are described which yield particles of approximately uniform size. With these hydrosol preparations, experiments have been made to test the validity of Svedberg's equation: $S = e^{k(t-t_0)}$, in which S represents the percentage concentration of the colloidal sulphur, t the temperature of the solution, k and t_0 constants which depend on the degree of dispersity of the hydrosol and the concentration of electrolyte in the solution (compare Abstr., 1909, ii, 309). For a given degree of dispersity, k is nearly independent of the concentration of the electrolyte (sodium chloride), whilst t_0 increases with the quantity of the coagulant. For a given salt concentration, k and t_0 diminish as the degree of dispersity of the hydrosol increases, the rate of diminution of t_0 being much greater than that of k. The addition of acids in small quantities reduces the value of t_0, whilst k remains unchanged. The validity of the exponential equation may be employed as a means of testing the uniformity of size of the particles of hydrosol. When particles of different sizes are present, this equation is incapable of representing the dependence of the equilibrium between the coagulum and the solution on the temperature.

The influence of temperature on the equilibrium which results when unequally granulated hydrosols are coagulated and of the degree of dispersity on the salt-fixing capacity of the coagulum are also discussed. H. M. D.

Coagulation of Copper Ferrocyanide. NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 136—138).—A chemically pure colloidal solution of copper ferrocyanide can be obtained by prolonged dialysis of the solution obtained in the interaction of copper chloride or sulphate and sodium ferrocyanide in equivalent proportions. The influence of various electrolytes on the coagulation of the negatively-charged colloidal particles has been examined in some detail. These experiments show that coagulation is determined by the cations, the nature of the anion having little influence on the coagulating power of the electrolytes. For cations of different valency this coagulating power increases with the magnitude of the electric charge. In the

case of the alkali metals, it increases with increasing atomic weight and with increasing velocity of diffusion of the cation. H. M. D.

Plasticity, Especially of Barium Sulphate. PAUL EHRENBERG (*Zeitsch. angew. Chem.*, 1911, **24**, 1957—1958).—Polemical against Atterberg (this vol., ii, 605), the author especially combating his views on the cause of plasticity. T. S. P.

Formation of Layers in Heterogeneous Systems. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 97—100).—If a system consisting of two different kinds of particles is acted on by an external force, which causes the two sets of particles to move with uniform speed, but with different velocities, a simple graphical consideration indicates that this motion must result in the setting up of a series of alternating strata. The stratification which is found when insoluble substances are formed as the result of the action of an aqueous solution of one substance on a solid jelly containing the second reacting component, can be explained satisfactorily by reference to the velocities of the reacting molecules or ions. The view that this stratification is due to the formation of supersaturated solutions is considered to be very improbable. H. M. D.

General Integrals of Chemical Kinetics. FERENCZ JÜTTNER (*Zeitsch. physikal. Chem.*, 1911, **77**, 735—743).—The integrals for the differential equation expressing the rate of reversible reactions are obtained, and certain deductions regarding the integrals of irreversible reactions and regarding chemical equilibria are given. G. S.

Equilibria in the Precipitation of Lead Carbonate. WALTER HERZ (*Zeitsch. anorg. Chem.*, 1911, **72**, 106—108).—Sodium carbonate solution has been shaken with several sparingly soluble lead salts at 25°, and the equilibrium determined by analysis. Equilibrium constants are obtained for the bromide, chloride, and sulphate.

C. H. D.

Reduction of Mercuric Chloride by Phosphorous Acid and the Law of Mass Action. JAMES B. GARNER, JOHN E. FOGLESONG, and ROGER WILSON (*Amer. Chem. J.*, 1911, **46**, 361—368).—It has been observed that the action of phosphorous acid on mercuric chloride proceeds very slowly in dilute aqueous solutions at the ordinary temperature. It was, therefore, considered of interest to determine the extent of the reaction, the effect of different temperatures and concentrations, and the order of the reaction.

The results have shown that at 25° and 30°, and at various concentrations, the reaction takes place in accordance with the equation $2HgCl_2 + H_3PO_3 + H_2O \longrightarrow H_3PO_4 + 2HgCl + 2HCl$. There is no equilibrium point, but the reaction proceeds to completion. It is demonstrated that the reaction is of the fourth order, and its velocity constant is therefore expressed by the equation:

$$K = 1/3t[1/(a-x)^3 - 1/a^3].$$

E. G.

The Composition of Solid Phases in Four Component Systems. JAMES M. BELL (*J. Physical Chem.*, 1911, **15**, 580—586. Compare Schreinemakers, Abstr., 1909, ii, 559).—Four component systems are qualitatively represented by a tetrahedral diagram in perspective. For quantitative purposes the space diagram must be projected on to two of the faces of the tetrahedron. For this purpose orthogonal projection and projection by lines parallel to one edge of the tetrahedron have been employed. The author discusses a method of "perspective" projection in which the lines radiate from the apex of the tetrahedron to project the curve on the base. The method, which is illustrated by reference to the system

$$H_2O\text{–}NaCl\text{–}BaCl_2\text{–}CuCl_2,$$

is more complicated than parallel projections. R. J. C.

The Thermal Analysis of Quaternary Systems. NICOLA PARRAVANO and G. SIROVICH (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 206—211).—The tetrahedral method of representation may be used for quaternary systems, each face representing one of the component ternary systems. The course of the eutectic lines and planes is traced in the simple case in which neither compounds nor solid solutions are formed. In the thermal analysis of such systems, mixtures may be so chosen as to lie on a plane passing through one edge of the tetrahedron and a given point, and the isothermals are then drawn on the isosceles triangle thus obtained. It is shown how these curves are utilised for the construction of the isothermal surfaces in the space-model. C. H. D.

Rates of Solution of Certain Metals in Dissolved Iodine and their Relation to the Diffusion Theory. RALPH G. VAN NAME and ROWLAND S. BOSWORTH (*Amer. J. Sci.*, 1911, [iv], **32**, 207—224. Compare Abstr., 1910, ii, 280).—Further measurements of the rates of dissolution of metals in aqueous solution of iodine containing dissolved iodides have been made, and these show that iron, cobalt, and nickel dissolve at the same rate as was previously found for cadmium, zinc, mercury, copper, and silver. From experiments with disks of cadmium, it is found that the rate of dissolution remains practically constant on the addition of sulphuric acid to the solution provided the acidity does not exceed $0\cdot1N$; when the acidity is further increased, the rate of dissolution diminishes. The rate at which cadmium dissolves is also dependent to a small extent on the nature of the dissolved iodide, and from the data for solutions containing potassium, cadmium, sodium, hydrogen, barium, lithium, magnesium, and calcium iodides, it appears that the velocity constants roughly correspond with what would be expected from the probable rates of diffusion of the corresponding tri-iodides.

Tin and magnesium dissolve more quickly than the other metals investigated. In the case of tin, this is supposed to be due to the primary formation of a stannous salt and the removal of iodine by the subsequent oxidation which occurs. The high velocity in the case of magnesium is probably due to the disturbing action of hydrogen bubbles which are evolved at the surface of the metal.

The results obtained are considered to support the view of Nernst that such dissolution processes are primarily determined by rates of diffusion. H. M. D.

The Velocity of Hydration of Metaphosphoric Acid. D. BALAREFF (*Zeitsch. anorg. Chem.*, 1911, **72**, 85—88. Compare Abstr., 1910, ii, 607, 951; this vol., ii, 107).—The velocity of hydration of metaphosphoric acid increases with the concentration of the aqueous solution in a linear manner, indicating that the hydration is accelerated by the metaphosphoric acid itself, and not by the hydrogen ions. C. H. D.

Course of the Intramolecular Transformations between *iso*Butyl and *tert.*-Butyl Bromides, and the Catalytic Actions Thereby Coming into Play. ROGER F. BRUNEL (*Annalen*, 1911, **384**, 245—271. Compare this vol., i, 413).—In furtherance of his object of ascertaining the change of free energy in reactions between organic compounds of comparatively simple structure, the author has determined the amounts of *iso*- and of *tert.*-butyl bromides existing in equilibrium at a high temperature (*loc. cit.*). The change of free energy, however, cannot be calculated from this equilibrium ratio without a knowledge of the course of the dissociation of the bromides into olefine and hydrogen bromide. Michael and Leupold (this vol., i, 250), amongst others, have examined this dissociation, and, stating it to be independent of the presence of catalysts, have introduced the conception of "static equilibrium" to explain their results. According to the author, this conception is unnecessary, since the dissociation of the bromides is not independent of the presence of catalysts. The apparatus used is described and figured. It is found that the velocity of dissociation of both bromides in the gaseous state, particularly that of *iso*butyl bromide, is largely influenced by the degree of cleanliness of the walls of the vessel, and also by the presence of the liquid phase. The presence of the liquid phase also influences, although to a smaller extent, the velocity of the intramolecular transformation of the one bromide into the other. In no case has the intramolecular transformation been observed without accompanying dissociation, and the author is of opinion that the dissociation is an essential intermediate stage of the transformation. C. S.

Velocity of Racemisation. WALTER HERZ (*Chem. Zentr.*, 1911, ii, 67; from *Jahresber. Schles. Ges. vaterland. Kult.*, 1911, reprint).—The rate of change of the optical rotation of hyoscyamine and scopolamine in the presence of bases was measured by Gadamer (compare Abstr., 1901, i, 605). The present author now shows that the rate at which racemisation occurs in these reactions is represented by the equation $kt = \log_e[a/(a-2x)]$, where a represents the initial concentration, and x the amount changed. The racemisation constant of hyoscyamine at 5° is for sodium hydroxide, $6{\cdot}5 \times 10^{-3}$, for tropine, $1{\cdot}9 \times 10^{-2}$; the constant of scopolamine at 2—4° is for sodium hydroxide, 0·77, for tropine, $1{\cdot}9 \times 10^{-2}$. This method may be used for the measurement of hydroxyl ion concentrations. G. S.

New Distillation Flask. ALFRED DAHLE (*Chem. Zeit.*, 1911, **35**, 1037).—A flask which is suitable for use in the distillation of fatty acids under reduced pressure is described. The neck of the flask is closed by a rubber stopper through which passes a glass tube, the lower end of which is widened out so as to nearly touch the neck of the flask. A capillary tube is fitted down the centre of this glass tube, whilst a side-tube on the neck of the flask carries a thermometer, and is provided with a second side-tube which is connected with the condenser. W. P. S.

Gas Generation Apparatus. GEORG PREUSS (*Chem. Zeit.*, 1911, **35**, 1131).—A modified Kipp's apparatus provided with extra large tabulures into which are ground wash-flasks. By the usual groove and hole arrangement these also serve as taps. L. DE K.

Tap for Hydrogen Sulphide Apparatus. JAMES H. WALTON, jun. (*J. Amer. Chem. Soc.*, 1911, **33**, 1586—1587).—A special form of tap is described, which cannot be left open by the student. It consists essentially of a strong spring pinch-clip which is fastened on to a board and closes the thick-walled rubber tube through which the gas is delivered. The clip is opened by pressing an iron lever, and on releasing the lever the supply is instantly cut off. The rate of flow is regulated by a screw pinch-cock situated at a higher point on the rubber tube. It is advisable to enclose the tap in a box, so that the student has access only to the end of the lever and about two inches of the end of the rubber tube. E. G.

An Extraction Apparatus. WALTER L. HALLE (*Biochem. Zeitsch.*, 1911, **36**, 245—247).—The apparatus, which is figured, is constructed of metal, and is capable of containing 2 kg. of material. It is of the ordinary Soxhlet pattern, but with two special features. About half way up the ascending limb of the syphon there is an additional tube with a tap. If the latter is opened, the liquid in the extractor will syphon off when it is only half full. On the descending limb of the syphon, near the bottom, there is another tube and tap; by opening the latter and fixing a tube to a condensor, the organic solvent can be distilled off. S. B. S.

Extraction Apparatus which Prevents the Formation of Emulsions. EMMANUEL POZZI-ESCOT (*Ann. Chim. anal.*, 1911, **16**, 382—383).—When a liquid is extracted with an immiscible solvent, the emulsion which is liable to form may be prevented by the use of a separating funnel, from which the air may be exhausted before the liquid and solvent are shaken together. The stopper of the tube is pierced with a hole, which, by rotating the stopper, may be placed in connexion with a small side-tube on the neck of the funnel; the air is exhausted from the funnel through this side-tube, the stopper is turned so as to close the funnel, the contents of the latter are shaken, and should any trace of emulsion result, this may be broken down by allowing air to enter the funnel suddenly. W. P. S.

Rapid Filtering Funnel. H. S[illegible] (*J. Amer. Chem. Soc.*, 1911, 33, 1584—1585).—The rate of filtration from an ordinary funnel can be increased to about two and a-half times the normal rate by etching deep lines extending from the apex of the funnel to points about two-thirds of the way up the sides. The grooves are not large enough to allow a filter paper to be broken by the stream from a wash bottle, but are sufficiently wide for the filtrate to flow down. Such funnels are particularly useful for filtering gelatinous precipitates.

E. G.

Automatic Filter. Marston L. Hamlin (*J. Amer. Chem. Soc.*, 1911, 33, 1584).—The apparatus described is designed for the filtration of large quantities of liquid containing a precipitate of such a character as to be capable of passing readily through the stem of a separating funnel. *It has been used in filtering* barium carbonate from large amounts of solution in the preparation of inositol.

A large separating funnel is placed on a ring-stand over an ordinary funnel containing a folded filter-paper, the lower end of the stem of the separating funnel being slightly above the apex of the paper. A tube passes through a rubber stopper in the neck of the separating funnel, and is led down so that its lower end is at the level at which it is desired to maintain the liquid in the lower funnel. The liquid is placed in the separating funnel, the stopper inserted, and the stopcock opened. The solution then runs into the lower funnel until it reaches the tube, and thus prevents the admission of air to the upper vessel. When the level in the lower funnel has fallen sufficiently, a small amount of liquid is siphoned over into the separating funnel and the lower one fills up again. E. G.

Method of Filling Reagent Bottles. James H. Walton, jun. (*J. Amer. Chem. Soc.*, 1911, 33, 1585—1586).—In order to enable students to fill their own reagent bottles with concentrated acids or other reagents without having to handle heavy bottles, a method has been devised by which the reagents are forced from the bottles by means of air-pressure. The bottles are placed on a table, two feet above which runs a pipe connected with the source of air-pressure. From this pipe valves are suspended by means of rubber tubing which fit into funnels which with delivery tubes are inserted through the stoppers of the bottles. The construction of these valves is described with the aid of a diagram. In the case of carboys, it has been found that the pressure required to force out the liquid is sufficient to drive out the stopper from the neck of the carboy, and a special arrangement has therefore been devised to prevent this. E. G.

Lecture Experiment: The Fermentation of Pyruvic and Oxalacetic Acids. Carl Neuberg and László Karczag (*Ber.*, 1911, 44, 2477—2479).—An application of the method already given (this vol., ii, 320, 520). W. J. Y.

Inorganic Chemistry.

Isomeric Inorganic Compounds. ADOLPH LAW VOGE (*J. Amer. Chem. Soc.*, 1911, **33**, 1563—1566).—During the compilation of an index of inorganic compounds according to their condensed formulæ, several new instances of isomerism and polymerism were observed. A list of these is now given, together with references to the papers in which the compounds are described. E. G.

Atomic Weight of Hydrogen. GUSTAVE D. HINRICHS (*Rev. gen. Chim. pure Appl.*, 1910, **13**, 351—354).—A review of the various determinations of the atomic weight of hydrogen which have been carried out since the time of Berzelius: the author considers that from the most trustworthy results the atomic weight of hydrogen must be 1·0078 (O = 16). F. M. G. M.

The Sand-Filtration and Precipitation of Chalk Waters. A. T. NANKIVELL (*J. Hygiene*, 1911, **11**, 235—258).—The ordinary submerged sand-filter bed is unsuitable for the purification of chalk waters. It removes micro-organisms, but favours the growth of algæ and other organisms. It can be made effective by the deposition of aluminium hydroxide on the surface of the sand, and it is best to exclude the light. The Porter Clark process is not only efficient for softening chalk waters, and also is an efficient steriliser; it is more effective than filtration through sand and aluminium hydroxide. W. D. H.

Amorphous Sulphur. VII. Freezing-point Curves of Liquid Sulphur on Separation of "Nacreous Sulphur" and Rhombic Sulphur Respectively. ALEXANDER SMITH and CHARLES M. CARSON (*Zeitsch. physikal. Chem.*, 1911, **77**, 661—676. Compare Abstr., 1903, ii, 139, 284; 1905, ii, 382, 580; 1906, ii, 157).—As there is no general agreement regarding the nomenclature of the different modifications of sulphur, the authors suggest the adoption of the symbols used by Muthmann. According to this, rhombic sulphur is represented by the symbol S_I, prismatic sulphur by S_{II}, the nacreous modification discovered by Gernez as S_{III}, and a fourth very labile monosymmetric modification (not further referred to in the paper) as S_{IV}. For mobile and viscous liquid sulphur the symbols S_λ and S_μ, which have met with general acceptance, are retained.

S_{III} can readily be obtained in lustrous, needle-shaped crystals by heating sulphur to a temperature exceeding 150°, then keeping at 98°, crystallisation being initiated by rubbing the inside of the tube with a glass rod.

For each of these modifications there is a freezing-point curve, depending on the relative proportions of S_λ and S_μ in the liquid with which the respective solids are in equilibrium. The respective freezing points when no S_μ is present are known as "ideal" freezing points, and are obtained by extrapolation. The ideal freezing point of S_I is

119·25°, of S_{II} 112·8°, and of S_{III} 106·8°. The "natural" freezing point of S_I is 114·5° (3·6% of S_μ), of S_{II} 110·2° (3·4% of S_μ), and of S_{III} 103·4° (3·1% of S_μ).

From the heat of fusion of monoclinic sulphur, as determined by Lewis and Randall (this vol., ii, 371), and the depression of the freezing point of S_λ due to S_μ, the conclusion is drawn that the formula of S_μ is S_8, which agrees with the vapour density determinations of Preuner and Schupp (compare Abstr., 1910, ii, 118).

With regard to some criticisms of Wigand (this vol., ii, 878) on the exact temperature of the equilibrium $S_\lambda \longrightarrow S_{II}$, the authors maintain the accuracy of their previous results.

G. S.

Metallographic and Photochemical Studies of the System Sulphur–Tellurium. MASUMI CHIKASHIGÉ (*Zeitsch. anorg. Chem.*, 1911, 72, 109—118 *).—Thermal analysis shows that sulphur and tellurium do not form a compound. Two series of solid solutions are formed, of very limited concentration, and the eutectic point lies at 109° and 7% Te (compare also Pellini, Abstr., 1909, ii, 726; Jaeger, *ibid.*, 1910, ii, 497). The transformation temperatures of sulphur at 400° and at 96·5° are lowered by tellurium. Whilst β-S holds 2% Te in solid solution, α-S retains only 0·5%, but the separation of the excess only takes place under the influence of light. Molten β-S dissolves 10% Te, and molten γ-S 20% Te. The precipitate obtained from solutions of tellurous acid and hydrogen sulphide, formerly supposed to be a compound TeS_2, is a mixture.

The solid solutions containing less than 0·5% Te are not sensitive to light. They include the Japanese red sulphur. The supersaturated crystals, containing from 0·5 to 2% Te, change from red to yellow or brown when exposed to light, the most active rays being $\lambda = 450$. The decomposed portions are more readily dissolved by carbon disulphide than the original crystals.

C. H. D.

Oxidation of Hydrazoic Acid [Azoimide]. HAROLD EATON RIEGGER (*J. Amer. Chem. Soc.*, 1911, 33, 1569—1576).—It has been shown by Browne and Shetterly (Abstr., 1909, ii, 658) that azoimide is produced in varying amounts by the oxidation of hydrazine in acid solution with different oxidising agents. Thiele (Abstr., 1908, ii, 940) has suggested that the lowness of the yields of azoimide obtained in this way by the action of certain oxidising agents is due to the ease with which azoimide itself undergoes oxidation. In order to test this hypothesis, experiments have now been made to ascertain the extent to which azoimide is oxidised in aqueous solution under conditions similar to those prevailing in the work on the oxidation of hydrazine.

The oxidising agents employed were (1) hydrogen peroxide, potassium chlorate, and potassium persulphate, which were found by Browne and Shetterly to oxidise hydrazine with formation of considerable amounts of azoimide; (2) potassium permanganate, manganese dioxide, and ferric oxide, which give but small quantities of azoimide under the same conditions; and (3) potassium iodate, which yields little or no azoimide.

* and *Mem. Coll. Sci. Eng. Kyoto*, 1911, 3, 197—210.

It has been found that of the reagents of the first class, hydrogen peroxide does not oxidise azoimide to an appreciable extent, potassium chlorate exerts a slight oxidising action, and potassium persulphate effects considerable oxidation. Of the oxidising agents belonging to the second class, potassium permanganate oxidises azoimide vigorously, manganese dioxide but slightly, and ferric oxide not appreciably. Potassium iodate does not oxidise the compound at all.

It is evident, therefore, that of the seven oxidising agents studied, only two, hydrogen peroxide and potassium permanganate, behave consistently with Thiele's explanation. A more satisfactory explanation is that proposed by Browne and Shetterly (*loc. cit.*), namely, that intermediate condensation products are formed during the oxidation, and that these decompose in different ways. E. G.

Theory of Silicates. Felix Singer (*Sprechsaal*, 1911, **44**, 52—54, 69—72).—A theoretical paper in which the author expresses his views on the constitution of some derivatives of felspar and other complex silicates, demonstrating the same by numerous graphic formulæ. The work of Pukall (Abstr., 1910, ii, 780), Thugutt, and Moroziewiecz is also discussed. F. M. G. M.

Preparation of Colourless Alcoholic Potassium Hydroxide. Hans Malfatti (*Zeitsch. anal. Chem.*, 1911, **50**, 692).—Potassium hydroxide is rubbed in a mortar with fully an equal amount of calcium oxide, a little alcohol being added to prevent irritating dust. The paste thus obtained is transferred by means of alcohol to a flask, which is then filled with alcohol. After frequent shaking, the liquid is allowed to clear and then siphoned off.

This solution keeps colourless for years, even in presence of air. The author attributes this to the fact that the treatment with calcium oxide removes traces of colloidal metals (copper and iron, for instance), which, as shown experimentally, may be the cause of the darkening of the solution. L. de K.

Double Salts Formed between Sparingly Soluble Sulphates and Alkali Sulphates. Maurice Barre (*Ann. Chim. Phys.*, 1911, [viii], **24**, 145—256. Compare Abstr., 1909, ii, 667, 733; 1910, ii, 710, 718, 781; this vol., ii, 42).—The results now given have been recorded previously in part (*loc. cit.*). The first portion of the paper is devoted to a study of the range of existence of the double salts of calcium, strontium, and lead with those of the alkali metals and ammonium. In the second portion a similar study is made of the double sulphates of (1) thorium and (2) cerium and lanthanum with the alkali metals, and a number of new compounds of this type are described in greater detail than before (*loc. cit.*). The solubilities of silver and mercurous sulphates in alkali sulphate solutions are also discussed.

At atmospheric temperature, and when less than 2·8% of potassium sulphate is in solution, no double salt is produced with calcium sulphate, but with more potassium sulphate, syngenite,

$$K_2SO_4,CaSO_4,H_2O,$$

is formed. This begins to be replaced at temperatures above 31°, by the compound $K_2SO_4,5CaSO_4,H_2O$ (van't Hoff and others, Abstr., 1904, ii, 561; 1905, ii, 319). With ammonium sulphate the compound $(NH_4)_2SO_4,CaSO_4,H_2O$ is alone stable at the lower temperatures; at 17° this begins to be transformed into $(NH_4)_2SO_4,5CaSO_4,H_2O$, and the latter gives place completely to $(NH_4)_2SO_4,2CaSO_4$ at 110°. The first begins to be transformed into the third directly at 76°. With sodium sulphate, sodium-syngenite, $Na_2SO_4,2CaSO_4,H_2O$, begins to form at 30°, and its range of existence is largely coincident with that of glauberite, $Na_2SO_4,CaSO_4$, and there is no definite point at which one passes into the other, the former being always in a metastable condition and liable to change into glauberite (van't Hoff, Abstr., 1900, ii, 284).

Strontium sulphate and lead sulphate form no double sulphates with sodium sulphate, and barium sulphate does not combine with sodium, potassium, or ammonium sulphate in the conditions observed in these experiments. The heats of formation of the double salts referred to are tabulated in the original, which also contains graphs illustrating the ranges of existence of the various compounds, drawn from data given in this and the previous papers (Abstr., 1909, ii, 667, 733).

The solubility of mercurous sulphate in water at 16·5° is 0·055%, and at 100° 0·092%, the quantities of free sulphuric acid formed at these two temperatures being 0·008% and 0·071% respectively (compare Drucker, Abstr., 1902, ii, 74). The residue obtained by repeatedly washing mercurous sulphate with water has the composition assigned to it by Gouy (Abstr., 1900, ii, 481), but as some metallic mercury is formed, the reaction must be more complex than is sometimes assumed. No double salt with potassium sulphate is formed.

From the data given previously (Abstr., 1910, ii, 718; this vol. ii, 42) it appears that thoria cannot be completely separated from ceria by treatment of the two sulphates with excess of potassium sulphate solution, since a too concentrated solution of the latter would precipitate both salts completely. Sodium sulphate solution would give a better, but still incomplete, separation. A 1% sodium sulphate dilution dissolves 3 to 4 grams of thorium sulphate, but only 0·02 gram lanthanum sulphate or 0·007 gram of cerium sulphate. Ammonium sulphate solution cannot be applied usefully to effect this separation.

T. A. H.

Potassium Barium Orthothioantimonate. EMANUEL GLATZEL (*Zeitsch. anorg. Chem.*, 1911, 72, 100—105).—Antimony pentasulphide and barium hydrogen sulphide yield barium orthothioantimonate. Solid potassium chloride is added to the solution in about four times the quantity required by the equation $2KCl + Ba_3Sb_2S_8 = 2KBaSbS_4 + BaCl_2$. In order to prevent oxidation during evaporation, a solution of potassium hydrogen sulphide is added. The double salt separates slowly, and may be recrystallised from water containing potassium hydrogen sulphide.

Potassium barium orthothioantimonate,

$$KBaSbS_4,6H_2O\ (K_3SbS_4,Ba_3Sb_2S_8,18H_2O),$$

forms colourless crystals which darken in air. When heated it melts, losing water, and solidifies on cooling to a crystalline mass.

C. H. D.

Preparation of Borax. II. MARIO G. LEVI and O. GARAVINI (*Gazzetta*, 1911, **41**, i, 756—781. Compare Abstr., 1910, ii, 501).—In the present paper the investigation of the reaction between boric acid and sodium chloride is continued, and the reactions between boric anhydride and sodium chloride and between boric acid and sodium sulphate are also dealt with.

From new experiments in which the temperature was raised only a little at a time, it is shown that, although the reaction between sodium chloride and boric acid has a greater velocity at 140° than at lower temperatures, yet it has begun at 120°, or perhaps even lower, so that it would seem that metaboric acid also is able to displace hydrochloric acid from sodium chloride. At 170° the reaction does not proceed so far in the presence of borax as it does when borax is absent, and the authors consider that this favours their hypothesis that a state of equilibrium is reached in the mixture. The equilibrium which is reached at 150° is not altered below 500°; between 500° and 600° a considerable evolution of free chlorine begins. Above 600° the limit of the reaction increases regularly, until at 1200° 75% of the sodium chloride is decomposed, or, if the heating at that temperature be prolonged, complete decomposition may occur. At the same time a loss of boric acid takes place which may reach 10%. The evolution of chlorine is less when the reaction is conducted in an atmosphere of nitrogen, but it is not abolished. Three possible causes of the evolution of chlorine are suggested: (1) oxidation of the hydrogen chloride favoured by catalytic action of the solids present, as in Deacon's process); (2) the presence of boric anhydride; (3) dissociation of the hydrogen chloride itself, which is found to begin at 800° under these experimental conditions.

The action of boric anhydride on sodium chloride is accompanied with a considerable evolution of chlorine, which increases with the temperature. The reaction seems to begin at 500° (5% of sodium chloride decomposed after four hours). In this case also the decomposition of sodium chloride is less in an atmosphere of nitrogen. It is suggested that the reaction in the presence of air may follow the equation: $2B_2O_3 + 2NaCl + O = Na_2B_4O_7 + Cl_2$.

The velocity of reaction between boric acid and sodium sulphate is much less than in the case of sodium chloride; after four hours at 1200° only 59% of the sulphate is decomposed. The reaction begins at 500°, that is, above the probable temperature at which pyroboric acid is converted into the anhydride. In agreement with this, it is found that the reaction proceeds at about the same rate when boric anhydride is taken instead of boric acid. The sulphuric acid is almost entirely decomposed at the temperature of the experiments, yielding sulphur dioxide.

R. V. S.

Melting Temperatures of Sodium and Lithium Metasilicates. F. M. JAEGER (*J. Washington Acad. Sci.*, 1911, **1**, 49—52).—Pure lithium metasilicate, prepared by repeatedly fusing

and grinding a mixture of lithium carbonate and quartz in the proper proportions, crystallises rapidly as glistening needles with D [illegible]. Its melting point, determined with the standard thermo-element of Day and Sosman (this vol., ii, 496), is sharply defined at [illegible], thus affording a suitable point (between copper, 1200°, and diopside, 1391°) for calibration purposes. Owing to under-cooling (to the extent of 100°) the solidification temperature is variable.

The solidification temperature of sodium metasilicate has been given by previous observers at various points ranging between [illegible] and 1056°. A nearly pure sample was found to melt at [illegible], but the temperature of solidification was disturbed by under-cooling.

L. J. S.

Lithium Silicates. II. R. Rieke and K. Endell (*Sprechsaal*, 1911, **44**, 97—99).—A continuation of previous work (this vol., ii, 490) on the physical and chemical properties of fused alkali silicates containing varying proportions of silica. The results are tabulated and exhibited in curves, whilst microphotographs illustrate the structure of the cooled substances.

F. M. G. M.

The Binary Systems of Magnesium and Calcium Chlorides with the Chlorides of Potassium, Sodium, Silver, Lead, Copper, Zinc, Tin, and Cadmium. Otto Menge (*Zeitsch. anorg. Chem.*, 1911, **72**, 162—218).—In the thermal analysis of mixtures of chlorides, it is necessary to use equal volumes of each mixture, as on account of the low thermal conductivity an alteration of volume does not cause a proportional change in the arrest time. A volume of 2·5 c.c. is used, enclosed in a tube of Jena glass. Mixtures containing magnesium chloride undergo partial decomposition, so that the solidified mass must be dissolved in water and the separated magnesium oxide estimated.

Magnesium and calcium chlorides form a eutectiferous series, with the eutectic point at 621° and 42·8% $CaCl_2$. Solid solutions are probably formed at the calcium end of the series. The freezing-point curve of mixtures of magnesium and potassium chlorides has two maxima at 485° and 437°, corresponding with the compounds $KCl,MgCl_2$ and $2KCl,MgCl_2$. This is confirmed microscopically. The curve for mixtures of magnesium and sodium chlorides has a eutectic point at 55% NaCl and 430°, and two breaks, indicating a compound $NaCl,MgCl_2$, and another of uncertain composition. Magnesium chloride forms simple eutectiferous series with silver, lead, cuprous, zinc, and stannous chlorides, the eutectic points, especially in the last two cases, being very close to the end of the diagram corresponding with the added chloride. Magnesium and cadmium chlorides are isomorphous, and give a continuous freezing-point curve.

Calcium and potassium chlorides give a freezing-point curve with a single conspicuous maximum, corresponding with the compound $KCl,CaCl_2$, m. p. 754°. The calcium-sodium chloride curve has a break at 600°, corresponding with the compound $4NaCl,CaCl_2$. The mixtures of calcium chloride with silver, lead, cuprous, zinc, and stannous chlorides closely resemble in their behaviour the mixtures

with magnesium chloride. Calcium and cadmium chlorides form a continuous series of solid solutions, the freezing-point curve showing a minimum, although the two salts are not isomorphous.

A comparison of the binary mixtures of the metals with those of the corresponding chlorides shows that when two metals of the group examined form intermetallic compounds, their chlorides do not combine, whilst metals which do not combine yield chlorides which form double salts. C. H. D.

The System Water-Calcium Chloride-Calcium Hydroxide at 25°. FRANS A. H. SCHREINEMAKERS and TH. FIGEE (*Chem. Weekblad*, 1911, 8, 683—688).—In this application of Schreinemakers' graphic method, two new oxychlorides of calcium, $CaO,CaCl_2,2H_2O$ and $4CaO,CaCl_2,14H_2O$, have been isolated. A. J. W.

Solubility of Zinc Oxide in Fused Lead Silicate and Borate. A. D. HOLDCROFT (*Trans. Eng. Ceramic Soc.*, 1909—1910, 9, 37—40).—An account of experiments in which varying quantities of zinc oxide were fused with lead silicate (litharge 78·8 parts, flint 21·2 parts) at 850° and 1000°, and the amount of zinc present in the fusions subsequently estimated; the lead silicate was also replaced by lead borate. The results indicated that at the lower temperature 7—10 parts of zinc oxide dissolved in 100 parts of lead silicate, and 50—60 parts of zinc oxide in 100 parts of lead borate, whilst at 1000° the solubilities were 13—14 and 60—70 respectively.

F. M. G. M.

Potassium Ammonoplumbite. EDWARD C. FRANKLIN (*J. Physical Chem.*, 1911, 15, 509—520. Compare Abstr., 1905, ii, 581).—Lead imide (PbNH), prepared by the action of potassamide on lead iodide in liquid ammonia, is soluble in excess of potassamide. From the solution, *potassium ammonoplumbite* with ammonia of crystallisation was obtained. The substance, recrystallised from liquid ammonia in absence of air, forms large, colourless crystals, with the composition $PbNK,2\frac{1}{2}NH_3$. On drying at 20°, efflorescence takes place, and the composition becomes $PbNK,2NH_3$. At 100° the ammonia is further reduced, and a chocolate-brown substance of formula $PbNK,NH_3$ remains. Above 100° no further loss of ammonia occurs, but at 140—145° the salt explodes.

The formula of the brown substance may be written $NH_2{\cdot}Pb{\cdot}NHK$ or $PbNH{\cdot}KNH_2$ or $HPb(\vdots NH){\cdot}NHK$. It is reconverted into the colourless variety on addition of ammonia. Potassium ammonoplumbite is discoloured by traces of air, and when exposed to the atmosphere or to water or dilute acids, explodes with violence. It is considered to be the ammonia analogue of potassium plumbite, although it has not been obtained free from the last molecule of ammonia of crystallisation. R. J. C.

Lead Silicates. PAUL WEILLER (*Chem. Zeit.*, 1911, 35, 1063—1065. Compare Hilpert and Nacken, Abstr., 1910, ii, 955).—The thermal analysis of mixtures of lead oxide and silica shows that

the metasilicate, $PbSiO_3$, is stable, but an orthosilicate is not formed. All mixtures containing more than 8% of silica yield a mass on cooling which is partly glassy and partly crystalline, whilst those containing from 12 to 32·5% SiO_2 form homogeneous glasses if rapidly cooled. Mixtures still richer in silica again show a tendency to crystallise, the glass being devitrified in parts.

The density curve shows a change of direction at the composition of the metasilicate, this compound being formed with expansion, and the further inclination of the curve points to the existence of a more acid silicate. The refractive index curve of the glassy mixtures shows a change of direction at the composition of the metasilicate.

The temperature at which reduction by hydrogen takes place is determined by observing the change of colour through a window in a vertical electric resistance furnace. This temperature remains constant at 240° in mixtures containing free lead oxide, but rises to 285° at the composition of the metasilicate, and again remains constant. C. H. D.

Crystallographic Observations on Cerium Sulphate Tetrahydrate. ARISTIDE ROSATI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 149—150).—Already quoted in a paper by Cingolani (Abstr., 1908, ii, 385). R. V. S.

Preparation of a Compound Containing Aluminium, Boric Acid, and Active Oxygen. CHEMISCHE FABRIK COSWIG-ANHALT (D.R.-P. 235050).—Compounds of aluminium and boric acid have previously been prepared. The *compound*, $Al_2Na_2B_2O_9,5H_2O$, containing 7—9% of active oxygen, was obtained by slowly treating a cooled solution of sodium aluminate (6·6 parts) with boric acid (5 parts) and 30 parts of a 10% solution of hydrogen peroxide; it forms a colourless powder, sparingly soluble in water, and gradually hydrolysed thereby, whilst it combines the disinfectant properties of both boric acid and hydrogen peroxide. F. M. G. M.

Thermal Analysis of Binary Mixtures of the Chlorides of Bivalent Metals. CARLO SANDONNINI and G. SCARPA (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 61—68. Compare this vol., ii, 800; Ruff and Plato, Abstr., 1903, ii, 588).—The paper deals with the thermal analysis of the systems $SnCl_2$–$PbCl_2$, $MnCl_2$–$CdCl_2$, $SnCl_2$–$CdCl_2$, $MnCl_2$–$SnCl_2$, and $MnCl_2$–$PbCl_2$.

The melting point of cadmium chloride is 568° (Ruff and Plato gave 598°); that of lead chloride is 495°, and that of manganese dichloride is 650°. Anhydrous manganese dichloride was prepared by heating the hydrated chloride in a current of dry hydrogen chloride; when heated in air it evolves chlorine, but in nitrogen it melts unchanged.

Stannous chloride and lead chloride give mixed crystals in all proportions, as also do cadmium chloride and manganous chloride.

The other pairs give simple eutectics; that of the system $SnCl_2$–$CdCl_2$ lies at 233° (90 mols. % of stannous chloride); that of the system $SnCl_2$–$MnCl_2$ is situated also at 233° (95 mols. % of

manganous chloride); that of the system $PbCl_2$-$MnCl_2$ lies at 408° (70 mols. % of lead chloride). R. V. S.

Further Ferro-magnetic Compounds of Manganese. EDGAR WEDEKIND and THEO. VEIT [with K. FETZER] (*Ber.*, 1911, **44**, 2663—2670. Compare Abstr., 1909, ii, 541)—*Manganese bismuthide*, MnBi, was obtained by the interaction of manganese thermite and bismuth. It forms octahedral and eight-sided columnar crystals, which are strongly magnetic; it is very sensitive towards acids, with the exception of concentrated hydrochloric acid, which reacts very slowly and may be used for purification. The same compound was also obtained, but with difficulty, by the direct fusion of the components in an atmosphere of hydrogen.

Manganese selenide, MnSe, was formed by heating manganese and selenium in an evacuated bomb-tube. It is crystalline in structure, weakly magnetic, and readily decomposed by water and mineral acids, hydrogen selenide being evolved. The *telluride*, MnTe, was prepared in a similar way, and has similar properties; it is crystalline, and has a silvery lustre.

Manganese silicide, Mn_2Si, was obtained from manganese thermite and silicon as a crystalline, greyish-black powder, which is relatively stable towards acids, and has hardly any magnetic properties. The *sulphide*, MnS, was also prepared by the alumino-thermic method; it is weakly magnetic, the magnetic properties becoming more pronounced on heating. The mineral alabandin behaves similarly. It has D[?] 3·9.

Manganese arsenide, was obtained by heating manganese and arsenic together. The resulting regulus was freed from manganese with dilute hydrochloric acid, and from excess of arsenic by heating in chlorine or bromine. A black, crystalline powder was left, which, on analysis, gave figures approximating to those calculated for MnAs. It was not pure, however, and on further heating in an electric oven, arsenic was lost and the compound Mn_2As formed (compare Hilpert and Dieckmann, following abstract). It is distinctly magnetic, in contradistinction to the arsenide first formed.

Manganese carbide cannot be prepared by the alumino-thermic method. The compound, Mn_3C, obtained in the electric furnace is magnetic.

The compounds of manganese with tervalent elements are the most strongly magnetic. T. S. P.

Arsenides. I. Iron and Manganese Arsenides. SIEGFRIED HILPERT and THEODOR DIECKMANN (*Ber.*, 1911, **44**, 2378—2385).—The authors find that the best method for preparing pure arsenides of the metals is to heat them at a high temperature with the vapour of arsenic under pressure. The finely-powdered metal and the arsenic are sealed up in an evacuated bomb-tube of Jena glass, and heated for several hours at 700—750°, a temperature much higher than the boiling point of arsenic. After cooling, the almost chemically pure arsenide can be mechanically separated from the arsenic which has

condensed on the walls of the tube, and is then readily purified by further treatment.

Iron arsenide, $FeAs_2$, after purification by treatment with dilute hydrochloric acid, was obtained as a silver-grey powder, which is probably microcrystalline. It is stable towards dilute and concentrated hydrochloric acid. The melting point, as determined by heating in a sealed quartz tube, lies between 980° and 1040°; D = 7·[illegible]. When heated at 680° in a current of hydrogen, the arsenide FeAs is obtained as a silver-white, crystalline powder. It is similar in its chemical properties to the diarsenide, and has m. p. 1020° and D = 7·[illegible]. Both these arsenides are completely non-magnetic.

Manganese arsenide, MnAs, could only be obtained in the pure condition when manganese prepared from the amalgam was used. Alumino-thermic manganese did not give satisfactory results (compare Wedekind, Abstr., 1907, ii, 353). It is a greyish-black powder, showing, apparently, no crystalline structure, D = 6·2; in its chemical properties it is similar to the iron arsenides. When heated in a current of hydrogen, arsenic is gradually volatilised, but no other compound is formed. It is strongly magnetic, but loses its magnetic properties when heated at 40—50°, the effect being a reversible one.

No evidence has been found for the existence of a compound Mn_2As (compare Wedekind, *loc. cit.*).

Phosphides may be prepared in a similar manner to the arsenides, and are to be reported on later. T. S. P.

The Internal Structure of Martensite and Pearlite. M. OKNOFF (*Metallurgie*, 1911, 8, 539—541).—The method of examining serial sections of steel (this vol., ii, 495) has been further applied, the thickness of the layer removed at each grinding being only 0·001 mm. The arrangement of ferrite and martensite in a steel containing 0·7% C, quenched from 750°, closely resembles that of ferrite and pearlite. Martensite, examined in a steel containing 0·5% C, quenched from 1000°, proves to be composed of plane lamellæ, 0·003—0·007 mm. broad, and only 0·001 mm. thick. Pearlite, examined in annealed steel, proves to be composed of curved, parallel lamellæ, about 0·001 mm. thick and of ten or twelve times that breadth. C. H. D.

Formation of Iron Carbonyl. A. STOFFEL (*Chem. Weekblad*, 1911, 8, 722—734).—An investigation of the conditions governing the formation of iron pentacarbonyl. Up to 60°, the influence of temperature on the reaction is slight, but just below 80°, adsorption of the reaction product by the iron at first retards the formation of the carbonyl, and finally inhibits it. Above 80° dissociation stops the action, so that large quantities in the state of vapour cannot be formed.

The presence of ammonia accelerates the combination of carbon monoxide and iron; that of hydrogen sulphide exerts no influence. A. J. W.

Peroxides. CARL TUBANDT and W. RIEDEL (*Ber.*, 1911, **44**, 2565—2570).—When a fine aqueous suspension of nickel peroxide is treated with dilute sulphuric acid, a solution is obtained which liberates iodine from potassium iodide, and decolorises permanganate to some extent. These reactions are not due to the formation of hydrogen peroxide (compare Tanatar, Abstr., 1909, ii, 484), which is not present even in traces, since its presence cannot be detected either with titanium dioxide or with chromic acid and ether. The authors are of the opinion that the liberation of iodine is due to the formation of persulphuric acid, or of Caro's acid, even in the dilute sulphuric acid used. The decoloration of the permanganate is only apparent, the colour being masked by the green colour of the nickel solution, as may be shown by experiments with nickel sulphate.

The formation of hydrogen peroxide when nickel peroxide acts on a solution of hydrocyanic acid in the presence of potassium cyanide is verified (compare Tanatar, *loc. cit.*). It is not formed from the nickel peroxide, however, but by the auto-oxidising action of the complex nickel cyanides formed. This is supported by the fact that nickel hydroxide, or any nickel salt, may be used in place of the peroxide.

There is thus no reason for placing nickel peroxide in a special class among the peroxides, and, moreover, the above results offer no support for Tanatar's views on the constitution of the peroxides. The work of Pellini and Meneghini (Abstr., 1909, ii, 506, 486) is not affected by the above.

T. S. P.

Nickel Peroxide and its Behaviour in Salt Formation. CARL TUBANDT and W. RIEDEL (*Zeitsch. anorg. Chem.*, 1911, **72**, 219—232. Compare preceding abstract).—The oxidation of nickel salts with various oxidising agents yields only precipitates of nickel peroxide. The product of the action of cold acetic acid on nickel peroxide is not, as supposed by Benedict (Abstr., 1906, i, 333), an acetate of tervalent nickel, but a colloidal solution of the peroxide, as is shown by ultramicroscopic investigation. Phosphoric acid forms very stable colloidal solutions of this kind. Concentrated phosphoric acid, on the other hand, forms a green solution, which contains the phosphorus analogue of Caro's acid (Schmidlin and Massini, Abstr., 1910, ii, 498). Benedict's nickelic sulphate is a nickelous solution containing Caro's acid, and the red colour observed by him in portions of the filtrate is due to the presence of manganese, which is oxidised to permanganic acid by the nickel peroxide.

Strongly cooled alcoholic solutions of acids yield with nickel peroxide dark red solutions, which prove, however, to be colloidal. In the electrolysis of nickel cyanide solutions between platinum electrodes, dark red solutions are obtained, which have reducing properties, and contain the suboxide, Ni_2O. The electrolysis of alkali carbonate solutions containing nickel between nickel plates, using a diaphragm, yields a dark solution which contains only the colloidal peroxide. All attempts to obtain nickelic salts have, therefore, been unsuccessful.

C. H. D.

Uranium Hexafluoride. OTTO RUFF and ALFRED HEINZELMANN (*Zeitsch. anorg. Chem.*, 1911, 72, 63—84).—Uranium hexahalides have not been prepared previously. The hexafluoride has now been prepared in three ways. Fluorine reacts with uranium pentachloride at $-40°$ according to the equation: $2UCl_5+5F_2=UF_4+UF_6+5Cl_2$. The two fluorides are separated by distillation. The course of the reaction suggests that uranium pentachloride is really a double compound, UCl_4,UCl_6. The pentachloride also reacts with dry hydrogen fluoride, forming a compound UF_6,xHF, which breaks up on distillation into UF_4 and UF_6. The difficulty of separation of the volatile hexafluoride from hydrogen fluoride makes this method a less useful one. Uranium carbide, UC_2, prepared at 2450° from uranium dioxide and carbon, yields only the tetrafluoride with pure fluorine, but in presence of chlorine at $-70°$ it yields the hexafluoride.

Uranium hexafluoride, UF_6, has the vapour density 11·7 (calc. 12·16) at 448° in a platinum vessel. The vapour pressure determined by Smith and Menzies' method (Abstr., 1910, ii, 1037) has also been determined at various temperatures, using 0·1 gram substance for each determination. The boiling point is 56·2°, and the calculated mean latent heat of evaporation between 42° and 57° is 29·4 cal. per gram, or 10,360 cal. per gram-molecule. The compound forms glistening, colourless or pale yellow, monoclinic crystals, m. p. 69·2° (corr.), at which temperature it has a vapour pressure of two atmospheres. It has $D^{20·7}$ 4·68

Uranium hexafluoride is highly reactive, attacking glass if traces of water are present, and reacting vigorously with water, alcohol, ether or benzene, depositing carbon in the last case. It reacts more slowly with carbon disulphide, paraffin, chloroform, and nitrobenzene. The best solvent is tetrachloroethane. It also reacts with nitric oxide, ammonia, and arsenic trichloride. It is reduced by most non-metals and metals, except gold and platinum. Sulphur forms US_2 and UF_4, together with a gas condensing at $-40°$ and freezing at $-135°$, which appears to be a new sulphur fluoride. C. H. D.

Vanadium Bromides. OTTO RUFF and HERBERT LICKFETT (*Ber.*, 1911, 44, 2534—2538).—The methods of preparation of the following compounds are based on those worked out for the vanadium chlorides (this vol., ii, 291).

If bromine vapour or, better still, a mixture of bromine and sulphur bromide vapour is passed over a mixture of vanadium pentoxide and sulphur at a red heat, the distillate does not consist of vanadyl tribromide, $VOBr_3$ (compare the corresponding chlorine compounds, *loc. cit.*), but of a product which, on being heated in a vacuum at 240°, leaves a residue of pure vanadyl dibromide, $VOBr_2$, sulphur bromide and bromine distilling away. If the temperature of the residue is raised to 360°, the vanadyl dibromide partly sublimes and partly decomposes with evolution of bromine, leaving a violet residue consisting of the hitherto unknown *vanadyl bromide*, VOBr. If this compound is further heated in a vacuum to 480°, vanadium tribromide distils away, leaving a residue of vanadium trioxide.

...adium tribromide is readily obtained by the action of bromine ...pours on vanadium carbide, V_4C_3, at a dark red heat.

Full details of the methods of preparation of the above compounds ...re given.

Vanadyl bromide, VOBr, crystallises in violet octahedra, and has ... 4·0002. It is only very slightly soluble in water, acetic ...hydride, ethyl acetate, and acetone. T. S. P.

Vanadium Fluorides. OTTO RUFF and HERBERT LICKFETT (*Ber.*, 1911, **44**, 2539—2549).—By the action of fluorine on vanadium ... on the vanadium chlorides, mixtures of vanadium fluorides were ...tained which could not be separated readily. Satisfactory methods ...r the preparation of the various fluorides by the action of anhydrous ...ydrogen fluoride on the anhydrous chlorides and bromides have, ...owever, been worked out.

When anhydrous hydrogen fluoride is passed over heated vanadium ...ichloride, a brown intermediate product is formed at 120—130°. At 310° the brown powder change to a green one, which still contains ...hlorine unless the passage of hydrogen fluoride is continued for six to ...ight hours and the temperature raised to a dark red heat. *Vanadium ...fluoride*, VF_3, is then left as a greenish-yellow powder, which is ...most insoluble in water and the usual organic solvents. The ...elting point lies above 800°, and it sublimes at a bright red heat; D^{19} 3·3628.

Vanadium tetrafluoride, VF_4, is produced by the action of anhydrous hydrogen fluoride on vanadium tetrachloride, the reaction being started at −28° and the temperature allowed to rise to 0° in the course of two hours. It is a brownish-yellow, loose powder, which is very hygroscopic, deliquescing in the air to a blue liquid; readily soluble in water (blue solution) and acetone (green solution); it has D^{23} 2·9749. Above 325°, it decomposes into vanadium pentafluoride and vanadium trifluoride.

Vanadyl difluoride, VOF_2, is prepared by heating vanadyl dibromide in a current of anhydrous hydrogen fluoride, first at 150—200° and then at 600—700° for six hours. It is yellow in colour, slightly soluble in acetone, but insoluble in other solvents; D^{19} 3·3956.

Vanadyl trifluoride, VOF_3, is prepared from vanadyl trichloride in a similar manner to that described for the preparation of vanadium tetrafluoride; it may also be obtained by heating vanadium trifluoride to a red heat in a current of oxygen. It forms yellowish-white crusts, and is very hygroscopic, deliquescing in the air to a brownish-yellow solution. At 132°, when heated in glass tubes, it decomposes, red vanadium pentoxide being deposited; it then melts at about 300° and boils at 480°. In a current of oxygen, it sublimes at 130°. It has $D^{20.5}$ 2·4591.

Vanadium pentafluoride, VF_5, is obtained as a pure white sublimate when the tetrafluoride is heated in a current of nitrogen, the temperature being gradually raised from 300° to 650°, and the latter temperature maintained for two and a-half hours. At the ordinary temperature, it possesses an appreciable vapour pressure, and in moist air becomes yellow, owing to the formation of oxyfluorides. It is readily soluble

in water, alcohol, chloroform, acetone, and light petroleum. When heated in sealed glass tubes it does not melt, even above 200°, but it readily attacks the walls of the tube. It has D^{19} 2·1766, and b. p. 111·2°/758 mm. It is the only vanadium compound in which five halogen atoms are bound to one vanadium atom.

Special methods were devised for the estimation of the vanadium and fluorine in the above compounds.

T. S. P.

The Action of Calcium Fluoride on Vanadium Pentoxide. Wilhelm Prandtl and Hermann Manz (*Ber.*, 1911, 44, 2582—2585). —When a mixture of vanadium pentoxide and calcium fluoride is heated to a red heat in an open platinum crucible, some of the vanadium is volatilised, the amount depending on the ratio $CaF_2 : V_2O_5$. When the ratio is 1 : 1, the loss is from 12% to 15%, and it increases to 30% with the ratio 5 : 1. If the crucible is covered with a lid, or with another crucible, which is kept cool during the heating, the latter is afterwards found to be coated with shining needle-shaped crystals of vanadium pentoxide, which are dark brownish-red when hot, and yellow when cold. Their formation is probably due to the volatilisation of a volatile vanadium fluoride or oxyfluoride, which is decomposed by the oxygen and water vapour of the air. This is made probable by the fact that when the reacting mixture is heated in a platinum tube in a current of nitrogen, an almost colourless, deliquescent sublimate is obtained. Analyses of the sublimate did not lead to any satisfactory conclusions; it contained quadrivalent vanadium. When the mixture is heated in a glass tube, the latter is strongly attacked, silicon tetrafluoride being formed.

T. S. P.

Tantalum, Tungsten, and Hydrogen. Adolf Sieverts and E. Bergner (*Ber.*, 1911, 44, 2394—2402).—Using the method previously described (Abstr., 1910, ii, 410, 851), the solubility of hydrogen in tantalum at varying temperatures up to 1330° has been measured. Under the same hydrogen pressure the solubility decreases with rise in temperature, and at a given temperature (above 450°) it is proportional to the square-root of the pressure. The solubility curve is very similar to that obtained with palladium and hydrogen, and quite different from the curves of copper, nickel, iron, cobalt, and platinum. With palladium and tantalum, the absorption is an exothermic process, whereas with the other metals it is endothermic. The order of solubility is much the same for tantalum and palladium.

When heated in hydrogen, tantalum wire undergoes a structural alteration, becoming brittle and crystalline (compare Pirani, Abstr., 1905, ii, 718), which properties it retains after the hydrogen has been extracted by heating in a vacuum.

Nitrogen reacts slowly with tantalum at temperatures above 900°, forming a nitride.

The solubility of hydrogen in tungsten is very small at temperatures up to 1500°, and the values obtained were not equilibrium values. Nitrogen does not react with tungsten, even at 1500°.

T. S. P.

Mineralogical Chemistry.

The Laws of Mineral Association from the Point of View of the Phase Rule. VICTOR M. GOLDSCHMIDT (*Zeitsch. anorg. Chem.*, 1911, **71**, 313—322).—The phase rule may be applied to mineral associations in the form: The maximum number of solid minerals that can co-exist in a stable condition is equal to the number of independent components contained in them. The number can only be exceeded at certain definite temperatures or pressures, at which transformations occur. The rule is applied to a number of mineral associations, including cases in which the components may unite to form binary or ternary compounds. An application to crystalline hornblendes of the Christiania region, derived from clays and limestone by contact-metamorphosis, shows the usefulness of the rule in determining which associations are possible, the components in this case being CaO, MgO, Al_2O_3, and SiO_2, whilst fifteen distinct minerals are possible, four of which may co-exist. C. H. D.

Bismuth Ores. EDUARD PRIWOZNIK (*Österr. Zeitsch. Berg. Hüttenwesen*, 1910, **58**, 713—716).—A bismuth ore for which the name *emplectite* is proposed contains S 19·10%, Bi 62·09%, and Cu 18·8%, with the empirical formula $Cu_2Bi_2S_4$ and D^{22} 6·223; it forms rhombic crystals, isomorphous with copper glance, and is found at Freudenstadt, in the Black Forest, in Norway, and at Dognaczka in Hungary.

Wittichenite has the formula $Bi_2Cu_6S_6$, D 6·006, and is obtained from Wittichen, in the Black Forest. A third copper bismuth ore, $2Cu_2S,3Bi_2S_3$, was described by Maderspach, but is not sufficiently characterised. F. M. G. M.

Hydrothermal Silicates. EMIL BAUR and F. BECKE (*Zeitsch. anorg. Chem.*, 1911, **72**, 119—161).—For the preparation of aqueous solutions of silicates at temperatures approaching a red heat, steel cylinders may be employed without a platinum lining, as the steel is only slightly attacked. The cylinder, with walls 18 mm. thick and a capacity of 11 c.c., is closed by means of a steel screw, rendered tight by a soft copper ring. The cylinder is only one-third filled with liquid, and is heated vertically in an electric resistance furnace. Each charge is exposed for 12 to 16 hours to a constant temperature of 350° or 450°.

The action of superheated alkaline solutions on crystalline quartz, alumina, etc., is very slow, and it is necessary to use amorphous materials. A clear solution is not formed, but the amorphous mass is converted into microscopic crystals without external change of form. The products are identified microscopically. The following minerals have been obtained, starting from silica, alumina, lime, and potassium or sodium hydroxide: Quartz, opal, orthoclase, albite, oligoclase, potassium faujasite, analcite, potassium nepheline hydrate, andalusite, pyrophyllite, muscovite, stilbite, gyrolite, and sodium and potassium

pectolite. The results are shown graphically on a diagram obtained from the tetrahedral representation of the quaternary system by drawing two planes through a point within the tetrahedron, each parallel with one face, and uniting the two triangles obtained in a plane.

The potassium faujasite contains much zeolitic water. Calcium aluminium silicates are not obtained under the conditions of the experiment, however the composition of the mixtures used is varied. The mixtures richest in alkali always yield zeolites, not felspars. Mixtures containing lime always yield pectolite. Leucite is not found under these conditions. Tridymite is also absent, and the modification of crystalline silica which occurs is always α-quartz. The andalusite obtained is possibly metastable, but transformation into sillimanite is not observed. It is probable that metastable phases are often present in zones of contact metamorphism. C. H. D.

Composition of Nephelite. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1911, 1, 109—112).—In the triclinic felspars are the well-known isomorphous molecules, $NaAlSi_3O_8$ (albite), $Ca_{\frac{1}{2}}AlSiO_4$ (anorthite), $NaAlSiO_4$ (carnegieite), and $KAlSi_3O_8$ (microcline); and there is a parallel series of monoclinic felspars. These compounds also form an isomorphous series of hexagonal modifications, namely: $NaAlSiO_4$ (essential component of nephelite; prepared artificially) and $KAlSiO_4$ (kaliophilite), to which may be added by analogy, $Ca(AlSiO_4)_2$ and $NaAlSi_3O_8$. The composition of nephelite can be very simply explained by the isomorphous mixing of these molecules; thus the recent analyses of Foote and Bradley (this vol., ii, 122) and of Morozewicz (Abstr., 1908, ii, 201) correspond very closely with:

	Foote and Bradley.	Morozewicz.
$NaAlSiO_4$	70·4%	74·7%
$KAlSiO_4$	19·0%	19·7%
$NaAlSi_3O_8$	10·6%	5·6%

L. J. S.

Minerals and Rocks of the Composition $MgSiO_3$–$CaSiO_3$–$FeSiO_3$. ROBERT B. SOSMAN (*J. Washington Acad. Sci.*, 1911, 1, 54—58).—The published analyses of pyroxenite rocks and pyroxene minerals are calculated to molecular percentages of the metasilicates and plotted on a triangle with $MgSiO_3$, $CaSiO_3$, and $FeSiO_3$ at the three corners, representing a three-component system. It is seen that the rock analyses all lie in a limited "eutectic field," with the rhombic pyroxenes on one side and the monoclinic pyroxenes on the other. The relations are in harmony with the experimental data of Allen and White (Abstr., 1909, ii, 247). L. J. S.

Physiological Chemistry.

Variations in the Response of Healthy Men to Dyspnœic Conditions Produced by Breathing a Confined Volume of Air. THEODORE HOUGH (*Amer. J. Physiol.*, 1911, 28, 369—390).—By breathing a confined volume (30 litres) of air, dyspnœa sets in, and healthy men attempt to secure increased ventilation of the lungs by increasing the rate or depth (or both) of the respiratory efforts. As a rule, rate and depth vary inversely; increase of rate occurred in five only out of twenty-five men. The employment of muscles of expiration is another variable factor. The facts described harmonise with the theory that the chief stimulus is the tension of carbon dioxide in the blood. W. D. H.

Gaseous Metabolism in Anaphylactic Shock. FRITZ LOENING (*Arch. exp. Path. Pharm.*, 1911, 66, 84—109).—In anaphylaxis, disturbances and lowering of heat-production and oxidation processes are always found. W. D. H.

Protein Cleavage Products in Expired Air. WOLFGANG WEICHARDT (*Arch. Hygiene*, 1911, 74, 185—193).—Tubercle bacilli pass into the expired air; it is therefore not improbable that decomposition products of bacilli, mucus, etc., do so also. By breathing into distilled water and evaporation of the water, a ponderable residue is obtained, which contains high molecular products of protein decomposition. Dissolved in normal salt solution, the biological test in mice in producing sensibilisation is obtained. Negative findings in the same direction by Inaba are criticised. W. D. H.

The Oxygen-transport Capacity of Blood Warmed to Different Temperatures. LEO VON LIEBERMANN and FRANZ WIESNER (*Biochem. Zeitsch.*, 1911, 35, 363—367).—From experiments on the rate of production of the blue colour with guaiacum-turpentine mixture, the conclusion was drawn that blood heated to different temperatures up to 50° is not appreciably altered in respect to its capacity to act as transporter of oxygen. At 50°, however, there may be some difference in respect to the capacity of taking up oxygen from the air, owing to the formation of methæmoglobin. S. B. S.

Chemical Studies in Blood Regeneration. ERNST MASING (*Arch. exp. Path. Pharm.*, 1911, 66, 71—83).—In anæmic rabbits and geese, characteristic changes occur in the phosphorised constituents of the blood which are believed to be related to regeneration of that fluid. In rabbit's serum, the phosphorus in the alcohol-ether extract is increased, and the red corpuscles are richer in phosphatides than normal. The nucleic acid in the red corpuscles is higher than normal in both anæmic rabbits and geese. Richness in nucleic acid and phosphatides is a mark of young corpuscles. W. D. H.

The Action of Choline on Blood-Pressure. Emil Abderhalden and Franz Müller (*Zeitsch. physiol. Chem.*, 1911, 74, 253—271).—Most observers agree that the typical action of choline is to lower blood-pressure, except in atropinised animals. Modrakowski and Popielski alone find that it raises arterial pressure, and attribute the results of others to impurities. The present research gives the results of choline injections under various conditions of narcosis, etc., and the outcome is that the typical action of choline is to lower pressure, and that the presence of impurities will not account for the differences observed. Some of the authors' preparation was sent to Popielski to test the matter, and he reported that it produced a rise of blood-pressure. Unfortunately for Popielski, the specimen sent (by mistake) was an impure specimen, which, according to him, should have produced a fall of pressure. It did produce a fall of pressure in Berlin, and so did the pure specimens. W. D. H.

Lactic Acid in Human Blood. H. Fries (*Biochem. Zeitsch.*, 1911, 35, 368—385).—A method is described in detail for estimating lactic acid in blood, of which the essential processes consist in precipitating the proteins by mercuric chloride in acid solution, extracting the protein-free solution with ether, converting the lactic acid thus extracted into a zinc salt, oxidising the latter with permanganate, and estimating the aldehyde thus formed by Ripper's bisulphite method. As a result it was found that lactic acid often occurs in human blood, but the average amount is not increased in fevers, and no conclusions can be drawn from the amount as to changes in the general metabolic processes. Lactic acid is increased after strenuous muscular work. Blood from the cadaver contains more lactic acid than that obtained from the living subject; the amount in the latter increases if it be incubated at 40° for two hours. There is no information available as to the origin of lactic acid in blood.

S. B. S.

The Fat of Dog's Blood under Normal and Various Experimental Conditions (Digestion, Hunger, and Phosphorus, Phloridzin and Chloroform Poisoning). Leone Lattes (*Arch. exp. Path. Pharm.*, 1911, 66, 132—142).—In normal dogs the light petroleum extract (Kumawaga-Suto's method), which contains higher fatty acids and cholesterol, varies between 0·3% and 0·42% of the blood, and is higher in venous than in arterial blood. This is doubled during absorption of food rich in fat, especially milk. It is also increased by poisoning with phloridzin and with phosphorus, and slightly in the early stages of inanition. Chloroform narcosis has practically no effect.

W. D. H.

The Distribution of Reducing Substances in the Blood of Mammals. H. Lyttkens and J. Sandgren (*Biochem. Zeitsch.*, 1911, 36, 261—265. Compare Abstr., 1910, ii, 785).—The blood-corpuscles of all the mammals investigated contain more or less the same amount of reducing substance, which is equivalent in reducing power to 0·05—0·08% dextrose, and varies slightly in the same species. It is

[no]t dextrose, however, as the reducing power remains intact after fermentation. The blood-serum contains, in the same animals, a reducing substance which is not dextrose, in amounts varying between 0·033 and 0·045% of dextrose equivalent. The dextrose itself, however, varies largely in the different animals, being 0·222% for rabbits, 0·148% for guinea pigs, and 0·291% for cats, whereas for man, pig, sheep, ox, and horse, it varies between 0·063 and 0·095%. It is assumed that in the smaller animals the ratio of body surface to body weight is large, and therefore the combustion is more intense; hence the larger amount of dextrose in the blood stream. The authors reply to some criticisms of Michaelis and Rona on their methods, giving certain experimental facts in their support. S. B. S.

Enzymatic Decomposition of Hydrogen Peroxide. GEORGE SENTER (*Zeitsch. physiol. Chem.*, 1911, 74, 101—103. Compare Abstr., 1903, ii, 661).—Waentig and Steche (this vol., i, 759) state that the decomposition of hydrogen peroxide by the enzyme of blood is not in general a reaction of the first order, as found by Senter and by Euler. The author points out that the conclusions of Waentig and Steche can only be regarded as valid when it is shown that the enzyme does not undergo oxidation during the reaction. G. S.

Passage of the Internal Secretion of the Pancreas of the Fœtus into the Blood of the Mother. ANTON J. CARLSON and FRED M. DRENNAN (*Amer. J. Physiol.*, 1911, 28, 391—395).—If a dog deprived of its pancreas becomes pregnant, or if a pregnant dog has its pancreas removed, pancreatic diabetes is lessened or prevented. This is due to the fœtal pancreas, the secretion of which passes into the mother's blood; this effect is most noticeable in the second half of gestation, when the fœtal pancreas is better developed and the Islands of Langerhans capable of playing their normal rôle. W. D. H.

The Presence in the Blood of the Pancreatic Internal Secretion. FRED M. DRENNAN (*Amer. J. Physiol.*, 1911, 28, 396—402).—Intravenous injections of fresh defibrinated blood from a normal dog into a dog deprived of its pancreas lowers the percentage of urinary sugar for a period of less than twenty-four hours. Control experiments show this must be due to the presence of the pancreatic internal secretion in normal blood. This is an unstable substance, and disappears when the blood is left a few hours. W. D. H.

Changes in Blood and Bone-Marrow Produced by Hæmorrhage and Blood-destruction. CECIL PRICE JONES (*J. Path. Bact.*, 1911, 16, 48—70).—After receiving 10 c.c. of a 1% solution of phenylhydrazine, the regeneration of red corpuscles in the rabbit is arrested or masked for at least six days. No such delay occurs after hæmorrhage. The cause of the delay is probably a toxic action on the bone-marrow. The type of regeneration is different in the two cases; the colour index is raised more by phenylhydrazine than by hæmorrhage, and the blood shows a higher grade of megalocytosis. W. D. H.

Hæmolysis by Ammonia. Ed. Stadler and H. Kleemann (*Biochem. Zeitsch.*, 1911, 36, 301—320).—By means of direct titration it is shown that the amount of ammonia taken up by blood-corpuscles after washing with saline follows the laws of adsorption phenomena, and in this way the conclusions of Gros are confirmed, who arrived at the same result by the measurement of the amount of hæmolysis. The adsorption is much slower if the experiments be carried out in isotonic sucrose instead of sodium chloride solutions. This is not due to the difference in the amount of the ammonia taken up, which is the same in both cases. In the case of blood-corpuscles in sucrose solution, the rate of hæmolysis is not constant, but sets in rapidly after a period during which but little hæmolysis takes place. In the case of blood-corpuscles in saline, the hæmolysis is a regular process. In the former case, the formula which expresses the relationship between the concentration of the ammonia and the time necessary for complete hæmolysis does not correspond with the laws of adsorption. The inhibitory influence of serum and peptone solutions on hæmolysis may be at least partly explained by the diminished adsorption of ammonia. When large amounts of blood-corpuscles are employed, the increased amount of ammonia adsorbed is not proportional to the increased quantity of blood, but diminishes with increasing amounts of it. Blood which has been in isotonic sucrose solution for twenty-four hours is more rapidly hæmolysed (and adsorbs more ammonia) than fresh blood.

S. B. S.

Hæmolysis by Acetic Acid. Ed. Stadler and H. Kleemann (*Biochem. Zeitsch.*, 1911, 36, 321—334).—The methods of experiment and the results obtained were similar to those in the case of ammonia (see foregoing abstract). In the case of acetic acid, the inhibitory influence of serum is very great, possibly owing to the combination of the serum with the acid.

S. B. S.

Hæmolytic Extracts of Organs. P. Schäfer (*Biochem. Zeitsch.*, 1911, 35, 445—470).—It has been shown that if hæmolytic soap solutions are heated with proteins, the hæmolytic substance will be carried down with the coagulum, which will then become hæmolytic, whilst the supernatant fluid will become inactive. It has been suggested that the hæmolysins in the organs are soaps, and it is now found that they act like soaps in respect to the action of proteins. Activated cobra venom acts also in the same way, although it cannot be carried down so completely by the proteins, and the protein-toxin combination is less stable.

Experiments were also carried out with the hæmolysin obtained by extracting the pancreas with alcohol. No regular results were obtained, as sometimes the extract from fresh tissues was inactive, and only became active after autolysis, whereas in other cases the reverse was observed. Neither could any connexion be traced between the state of nutrition or the quality of the food (that is, whether the diet had been mainly protein, carbohydrate, or fat) on the hæmolytic power of the alcoholic pancreas extract; soap injected into the blood-stream of an animal rapidly disappears, as the injection causes so

appreciable increase in the hæmolytic power of the serum removed a short time after the injection. S. B. S.

Relation of the Reaction of the Culture Medium to the Production of Hæmolysin. E. E. ATKIN (*J. Hygiene*, 1911, 11, 193—201).—Bacteria differ greatly in their range of growth in bouillon of varying reactions. Roughly, the optimum of growth occurs when the reaction is neutral to phenolphthalein; but most micro-organisms have some power of overcoming the inhibitory effect of sodium hydroxide; the capacity to overcome the effect of hydrochloric acid is rarer. The production of hæmolysin by *Vibrio nasik* is not limited to an optimum reaction, but is coextensive with its range of growth in media of varying reactions, but the maximum is reached sooner and lost sooner in alkaline as compared to acid cultures.

W. D. H.

The Alterations in Hæmolytic Immune-substance which Occur During Immunisation. CARL H. BROWNING and G. HASWELL WILSON (*J. Hygiene*, 1911, 11, 208—219).—Rabbits were injected intraperitoneally with the red corpuscles of ox-blood; the immune-substance in the serum at an early stage is deficient in the power of causing absorption of complement; in later stages this is not the case. W. D. H.

Effects of Ultra-violet Rays on Serum. W. M. SCOTT (*J. Path. Bact.*, 1911, 16, 148).—The exposure of anti-toxic serum to ultra-violet rays destroys the major part of the antitoxin, but leaves the anaphylactic toxicity still appreciable. The procedure also renders the serum incoagulable by heat, and markedly increases the amount of protein precipitable by half saturation with ammonium sulphate.

W. D. H.

A Reversed Action of the Chorda Tympani on Salivary Secretion. HENRY H. DALE and PATRICK P. LAIDLAW (*J. Physiol.*, 1911, 43, 196—198).—Several observers have noted the reversal of effects of stimulation of nerves after certain drugs. The present paper draws attention to the effect of cytisine, the alkaloid of laburnum seeds, which has an action similar to that of nicotine in reversing or lessening the usual action of stimulation of the chorda tympani nerve. W. D. H.

Lecithin and Diastatic Action. EMILE F. TERROINE (*Biochem. Zeitsch.*, 1911, 35, 506).—In view of the recent investigations on this subject, the author reiterates his conclusions, namely: (1) Lecithin does not increase the rate of hydrolysis of monobutyrin by pancreatic juice, and increases only to a slight extent in more concentrated solution the rate of hydrolysis of oils. (2) It increases the lipolytic action of neither mucous membrane of stomach (in glycerol) nor intestinal lipase. (3) It has no action on the rate of hydrolysis of starch, the digestion of caseinogen or coagulated albumin, or the coagulation of milk by pancreatic juice. S. B. S.

Physiology of Digestion. III. The Secretion of Gastric Juice when the Chlorine Supply of the Body is Lessened. Rudolf Rosemann (*Pflüger's Archiv*, 1911, **142**, 208—234. Compare Abstr., 1907, ii, 706; 1910, ii, 1082).—Three experiments on dogs show that the secretion of gastric juice varies directly as the condition of nutrition in the animal; further, the supply of chlorine is most important, not only on the amount of acid in the juice, but for the secretion of the juice at all. The secretion commences again on giving chlorides. About 20% of the chlorine supply in the food is available for gastric juice secretion. W. D. H.

The Preparation of Solutions of Rennet Poor in, or Free from, Pepsin. Olof Hammarsten (*Zeitsch. physiol. Chem.*, 1911, **74**, 142—168).—A contribution to the vexed question of the identity or non-identity of the gastric enzymes. The main result of the research is that by precipitation of an acid infusion with caseinogen, the relation of the two enzymic actions is completely altered; the peptic is much more diminished than the rennetic. There can be no question here of the harmful action of reagents on the enzymes. The weakening of peptic activity cannot again be due to the appearance of inhibitory substances, but is only explicable on the assumption that the filtrate is poor in pepsin. From this it follows that the two enzymes are distinct, pepsin being precipitated with the caseinogen in greater proportion than rennin. W. D. H.

The Specific Inhibition of Rennet, and Differences between Rennets. Sven G. Hedin (*Zeitsch. physiol. Chem.*, 1911, **74**, 242—252).—By warming neutral infusions of the gastric mucous membrane of guinea-pig, calf, and pike with dilute ammonia and then neutralising, substances are formed which inhibit rennetic action. The inhibitory substances only inhibit the rennet of the animals used. The specific action of the inhibitory substances indicates that the enzymes they inhibit are specific also. W. D. H.

Digestive and Absorptive Defects. I. E. S. London, W. F. Dagaeff, B. D. Stassoff, and O. J. Holmberg (*Zeitsch. physiol. Chem.*, 1911, **74**, 328—359).—After removal of the whole or part of the stomach, various motor disturbances in the rest of the alimentary canal are noted, which are described in detail. The disturbances of secretory activity vary in relation to the sort of food given. Among the points mentioned are: (1) that protein and not fat leaves the stomach first after partial removal, and (2) that the duodenum enlarges into a reservoir when the excision is complete. Resection of the ileum leads to increased activity of the upper portion of the tube both as regards digestion and absorption, whereas resection of the jejunum produces a compensatory action in the large intestine. Obliteration of the pancreatic vessels produces little or no effect on digestion, and the same is true for occlusion of the pancreatic ducts. Total removal of the pancreas appears to evoke no compensatory activity. W. D. H.

Effects of Nutrition with Maize. III. Action of the Pancreatic Juice of the Dog on Zein and Gliadin. SILVESTRO BAGLIONI (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 36—39. Compare Abstr., 1910, ii, 625).—Zein and gliadin are digested by pancreatic juice in the same way as animal protein. The biuret reaction in the intermediate stage of the process shows the presence of peptones, and later of amino-acids. From comparative experiments in which the free amino-acids formed were estimated by Sörensen's method, it is shown that gliadin is more readily digested than zein. R. V. S.

The Detection of Active Pepsin in the Intestinal Contents by means of Elastin. EMIL ABDERHALDEN and OTTO MEYER (*Zeitsch. physiol. Chem.*, 1911, 74, 67—100).—By means of adsorption with elastin, pepsin is always discoverable in the small intestine in important amounts. Peptic digestion is not confined to the stomach; the individual parts played by pepsin, trypsin, and erepsin in this part of the alimentary canal in protein digestion have still to be cleared up. It is perhaps their joint action which leads to the rapid disintegration of proteins into their amino-acids. The pepsin is no doubt adsorbed by elastin and connective tissues in the stomach, and carried thus in an active condition into the intestine.

W. D. H.

The Use of Elastin for the Detection of Proteolytic Enzymes. EMIL ABDERHALDEN and KARL KIESEWETTER (*Zeitsch. physiol. Chem.*, 1911, 74, 411—426).—Elastin absorbs enzymes, as Grützner showed that fibrin does; its special value is that it itself only very slowly undergoes any cleavage. By its use, the following facts were determined: (1) The fæces of ox, horse, dog, and man usually contain no digestive enzymes; (2) peptolytic enzymes were detected by the optical method and the biuret reaction in the following organs, or juices: horse liver, the juice from horse liver, the juice expressed from yeast, and horse's kidney. Some observations on the comparative digestibility of elastin, fresh egg-white, and boiled egg-white are given. The effects are not the same with the natural and artificial gastric juice. W. D. H.

Chemistry of Digestion and Absorption in the Animal Body. XL. The Degree of Cleavage of Different Proteins in the Alimentary Canal. E. S. LONDON and A. G. RABINOWITSCH (*Zeitsch. physiol. Chem.*, 1911, 74, 305—308).—Gastric digestion has only a limited power to cleave proteins into peptides; this power increases in the intestine. The amount of cleavage varies with different proteins, but there is no difference whether the proteins are obtained from the same species of animal or not. W. D. H.

Chemistry of Digestion and Absorption in the Animal Body. XLI. The Digestion of a Mixed Diet in Dogs and Men. R. S. KRYM (*Zeitsch. physiol. Chem.*, 1911, 74, 312—317).—In dogs, absorption of the chyme is most active at early stages of digestion, but it increases again a little at the end. Carbohydrates

are absorbed first, then nitrogenous substances, and fats most slowly. In man some few observations show that absorption is similar to that in the dog. W. D. H.

A Reversible Phenomenon in the Action of Intestinal Juice on the Products of Casein Digestion. E. S. London (*Zeitsch. physiol. Chem.*, 1911, **74**, 301—304).—The intestinal chyme after feeding on casein is jelly-like; on removal from the body it becomes fluid in a few days under antiseptic conditions. The jellying is due to enzyme action, and is directly proportional in its velocity to the amount of intestinal juice; it runs parallel to the rate of formation of peptides, and is hastened by sodium carbonate. Its subsequent liquefaction is due, not to intestinal, but to other enzymes. The phenomenon is similar to plastein reactions. W. D. H.

The Action of Intestinal Juice on the Digestive Products of Various Proteins. E. S. London and S. K. Solowéeff (*Zeitsch. physiol. Chem.*, 1911, **74**, 309—310).—No single protein was found to be entirely decomposed by intestinal juice into peptides; the amount of cleavage was least for elastin; casein, gliadin, horse-flesh, gelatin, and dog's plasma follow in the order named. W. D. H.

The Specific Adaptation of the Digestive Juices. IV. The Relative Amount of Enzymes in the Intestinal Chyme on Different Diets. E. S. London and R. S. Krym (*Zeitsch. physiol. Chem.*, 1911, **74**, 325—327).—No adaptation of the amount of enzymes to the amount of the kind of food given was found to occur in the intestine; indeed, lipase is in excess when pure protein food is given. W. D. H.

Ereptase of the Intestinal Juice. Giuseppe Amantea (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 74—78).—The author has experimented with the secretion of isolated portions of the intestine of the dog produced with the aid of various mechanical and chemical stimuli. The juice is allowed to act on solutions of Witte's peptone or of Merck's casein, and the quantity of amino-acids formed is estimated by Sörensen's method. It appears that the secretion of the intestine proper does contain an ereptase. Differences can be observed between the activity of the secretions obtained with different stimuli, but they are not very marked, and the juice collected under the action of one and the same stimulus may exhibit considerable variation. The quantity of amino-acids produced is greater from peptone than from casein in almost all cases. R. V. S.

The Laws of Digestion and Absorption. X. The Disappearance of a Solution of Dextrose from the Stomach. E. S. London and W. F. Dagéeff (*Zeitsch. physiol. Chem.*, 1911, **74**, 318—321).—The emptying from the stomach of a 5% solution of dextrose follows the formula $x=k\sqrt{M}/(t+p)$, where p is Mk [illegible] and k is 10·35. The stomach empties in from thirty to sixty minutes. W. D. H.

The Laws of Digestion and Absorption. XI. Absorption of Proteins and Carbohydrates. E. S. LONDON and O. E. GABRILOWITSCH (*Zeitsch. physiol. Chem.*, 1911, 74, 322—324).—The quantity of carbohydrate and protein absorbed is directly, and of water indirectly, proportional to the square-root of the quantity present, unless the concentration is abnormally great. The quantity of intestinal juice (N) which is secreted in dextrin-digestion varies directly with the square-root of the substance (M) dissolved: $N = k\sqrt{M}$; $k = 0{\cdot}1755$.
W. D. H.

The Bleaching of Flour. J. M. HAMILL. **Chemical Changes Produced in Flour by Bleaching.** GORDON W. MONIER-WILLIAMS (*J. Hygiene*, 1911, 11, 142—166, 167—187).—These papers are abstracts of Local Government Board reports. The first is mainly technical, the second deals at greater length with the chemical changes produced, and the effect of bleaching on the digestibility of flour and bread. The digestibility of bleached flour is reduced. Salivary digestion was especially investigated. W. D. H.

Carbohydrate Metabolism and Glycosuria. FREDERICK W. PAVY and WILLIAM GODDEN (*J. Physiol.*, 1911, 43, 199—208).—Dextrose absorbed from the alimentary tract or intravenously injected in rabbits becomes fixed, and does not show itself either in blood or urine. This power of fixation is not unlimited, and is less when the sugar is injected rapidly, or when the amount of sodium chloride in the blood is increased. The fixing capacity, it is suggested, is due to bioplasmic incorporation carried out by lymphocytes, leucocytes, and growing bioplasm on other cells. W. D. H.

Carbohydrate Metabolism. II. The Prevention and Inhibition of Pancreatic Diabetes. FRANK P. UNDERHILL and MORRIS S. FINE (*J. Biol. Chem.*, 1911, 10, 271—285. Compare this vol., ii, 910). —Removal of the pancreas from a dog may be followed by glycosuria within two hours. This is prevented by previous injections of hydrazine. The effect of a single hypodermic injection of 50 mg. of hydrazine sulphate per kilo. of body-weight may last two to four days. The amount of blood sugar in animals so treated and depancreatised is below the normal, or is at any rate not increased. If the injection is made during the course of pancreatic diabetes, the excretion of sugar in the urine is completely inhibited. After the administration of hydrazine, the presence of adrenaline in the adrenal bodies may still be demonstrated. In this respect hydrazine differs from phosphorus. The tentative hypothesis advanced can only be fully understood by the full presentment of it in the original paper; the underlying assumption, however, is that there exists an inter-relation between the pancreas, liver, and adrenals which normally keeps the amount of blood sugar constant. When the pancreas is removed, facilitation of carbohydrate katabolism is lost, and the opposing effect of the adrenals has full sway. Hydrazine, like phosphorus, is considered to diminish adrenal activity. W. D. H.

The Importance of Lipoids in Nutrition. WILHELM STEPP (*Zeitsch. Biol.*, 1911, **57**, 135—170).—If mice received food freed from lipoids by alcohol and ether, they died in a few weeks. This is not due to alteration in the saline constituents, or to the removal of fats. Fat added to the extracted food does not delay the fatal result; the addition of the alcohol-ether residue does. The important materials are lipoids, and are contained in the milk plasma. Lecithin and cholesterol alone are not the materials in question. Boiled milk supports life in mice as well as unboiled; but food free from lipoids *plus* boiled milk, killed half the mice used; if unboiled milk is used instead, health remains perfect. W. D. H.

The Action of Some Non-protein Nitrogenous Compounds on Nitrogenous Metabolism of the Carnivora with Special Reference to Ammonium Acetate. ERNST PESCHECK (*Pflüger's Archiv*, 1911, **142**, 143—207).—If ammonium acetate is added to the food of dogs, even in comparative small amount and for a short time, the nitrogen is utilised. If it is intravenously injected, it has a strongly stimulating action, leading to noteworthy loss of nitrogen from the body. Ammonium tartrate has a harmful effect on nitrogenous metabolism. Asparagine caused nitrogen retention, but in a second experiment on the same dog, this was not confirmed.

W. D. H.

The Value of Different Amino-acids in the Organism of the Dog under Different Circumstances. EMIL ABDERHALDEN, ALBERTO FURNO, ERICH GOEBEL, and PAUL STRÜBEL (*Zeitsch. physiol. Chem.*, 1911, **74**, 481—504).—Knoop has shown that in the dog, β-benzylpyruvic acid is transformed into anilinobutyric acid. This opens up the possibility of the transformation of one amino-acid into another, and thus the elucidation of many metabolic problems. As a preliminary to further work on such lines, the effect on the urine of fasting dogs was investigated; the principal experiments recorded in the present paper deal with glutamic and aspartic acids, asparagine and histidine; these were given alone or in conjunction with sucrose or pyruvic acid. The results given in full tables are very inconstant; sometimes even with the same substance there was a fall, sometimes a rise, either in total nitrogen, ammonia-nitrogen, or amino-acid nitrogen of the urine. As a rule, there was no appreciable effect at all, and the changes where they do occur are very slight.

W. D. H.

Creatine and Creatinine. I. The Rôle of the Carbohydrates in Creatine-Creatinine Metabolism. LAFAYETTE B. MENDEL and WILLIAM C. ROSE (*J. Biol. Chem.*, 1911, **10**, 213—264).—A carbohydrate diet, absolutely nitrogen- and fat-free, produces a marked reduction in the elimination of total nitrogen and creatine in fasting rabbits. If it is continued for two or three days, creatine disappears from the urine. Alcohol produces no decrease; a pure fat diet produces no decrease; and a diet of mixed fat and protein also causes no reduction in creatine elimination. An increase in the elimination of total

creatinine (that is, creatine *plus* creatinine) is always accompanied by an increase in the output of total nitrogen; it does not follow that the reverse is true; carbohydrates, in contrast to other foodstuffs, prevent the excretion of creatine, and are therefore indispensable for normal creatine-creatinine metabolism. The parallelism of total creatinine and total nitrogen output in inanition and with nitrogen-free diets is ascribed to a common source, namely, tissue or endogenous metabolism. The metabolism of exogenous or reserve protein is not accompanied by a production of creatine or creatinine. The intimate relation of creatine excretion (or the failure of its conversion into creatinine) to carbohydrate metabolism is discussed in full; experimental interference with the latter (such as phloridzin poisoning, which depletes the carbohydrate store, or phosphorus poisoning, which disturbs the glycogenic function) leads in dogs to an increased output of creatine. W. D. H.

How far can Protein Katabolism in Inanition be Diminished by Feeding on Carbohydrates? W. WIMMER (*Zeitsch. Biol.*, 1911, 57, 185—236).—The experiments were performed on dogs, and it was found that feeding on carbohydrates can effect a sparing of protein to the extent of 55%; this is greater than the effect of gelatin. Starch and dextrose are about equal, provided the intake is divided into several meals per day. Pathological conditions appear to affect the result. W. D. H.

Protein Metabolism in the Dog. CHARLES G. L. WOLF and EMIL ÖSTERBERG (*Biochem. Zeitsch.*, 1911, 35, 329—362).—The changes produced in the metabolism by giving quantities of protein, carbohydrate, and fat respectively insufficient for the body needs to a starving dog were investigated, the nitrogen and sulphur output and the distribution of these elements amongst various constituents by the urine being determined. It was found that the protein ingestion covers the sulphur lost by the body far more effectively than the nitrogen loss, and, in fact, in one case it was found that the body was retaining sulphur whilst losing nitrogen. The ratio of the amide- and urea-nitrogen to the total, tends to increase when protein is ingested; the ammonia-nitrogen remains more or less proportional to the total nitrogen. The creatinine-nitrogen is not affected, except that it appears to be somewhat less during the first period of protein ingestion than during starvation. The creatine appears on the third day of starvation, and disappears after ingestion of carbohydrates and proteins, but not of fat. The ratio of the residual nitrogen to the total diminishes after protein ingestion. The ratio of total sulphuric acid to total sulphur increases as the output of the latter increases in the urine; for example, after protein ingestion. The ethereal sulphur is independent of the food, and has no relationship to the indican excreted. Carbohydrate ingestion after starvation decreases the amide- and urea-nitrogen ratio, but increases the ammonia-nitrogen ratio. Like proteins, carbohydrates cause a disappearance of creatine. They also cause an increase, both absolute and relative, of the residual nitrogen and sulphur. Ingestion of fat hardly alters the distribution

of the nitrogen, as compared with what exists during absolute starvation. S. B. S.

Metabolism of Development. III. Qualitative Effects of Pregnancy on Protein Metabolism in the Dog. JOHN R. MURLIN (*Amer. J. Physiol.*, 1911, **28**, 422—454).—In pregnancy nitrogen is retained, and the urea and ammonia in the urine are relatively low, the nitrogen which would normally be excreted in these forms being re-synthesised to make good the depletion of the blood proteins caused by the product of conception. The creatinine, uric acid, and undetermined nitrogen show in consequence a relative increase. The same is true for sulphur; the inorganic sulphate in the urine is decreased, being held back for fœtal development, and the "neutral sulphur" increased. On the days preceding parturition, creatine was found in the urine; this is indicative of tissue changes in the uterus. W. D. H.

The Influence of the Various Components of Diet and of the Ingestion of Various Iron Preparations on Iron Metabolism. MARTIN KOCHMANN (*Biochem. Zeitsch.*, 1911, **36**, 268—274).—The experiments were carried out on the same lines as the previous work of the author on calcium and magnesium metabolism. Dogs were fed on meat diets containing a known quantity of iron. The effect on the iron metabolism of increase of proteins, or of the addition of sugar and carbohydrates to the meat diet, was investigated. The addition of all these constituents of diet to the original diet appeared to exert an unfavourable influence, in that it increased the negative balance. The minimal quantity of iron necessary for iron equilibrium depends therefore on the quantity and character of the diet. The administration of ferratin, metaferrin, and ferric phosphate can influence the iron metabolism favourably, converting a negative into a positive balance, or increasing a positive balance where this previously existed. No marked difference can be definitely stated to exist in the action of the three iron preparations, although the organic preparations appear to exert a more favourable influence. S. B. S.

The Heat Production in the Vital Oxidative Processes of Eggs I.—III. OTTO MEYERHOF (*Biochem. Zeitsch.*, 1911, **35**, 246—279, 280—315, 316—328).—In view of the study of the relationships between various morphological changes (membrane formation, bifurcation, etc.) produced in the eggs of sea urchins and other animals by both natural and artificial causes (fertilisation, treatment with narcotics, hypertonic solutions, etc.), and the amounts of oxygen utilised under different conditions, by Loeb and by Warburg (this vol., ii, 211), the author undertook the study of the amounts of heat produced under various conditions. The eggs were placed in a Dewar flask kept in a thermostat, and the heat changes during the vital process were measured by a Beckmann thermometer immersed in the vessel. Details are given as to the method of determining the calorimetric water value of the vessel, and of the various corrections to be applied, and the apparatus is figured. The oxygen used up was estimated in a second vessel kept

in as nearly as possible under the same conditions as the first, with addition of a known quantity of eggs, a modification of Winkler's method being employed for this purpose.

The nitrogen in the eggs was determined by Kjeldhal's method, and the results expressed in terms of calories developed per hour per 140 mg. of nitrogen. It was found that, in the case of sea-urchin's eggs after fertilisation, this was 4·0—4·2 calories in the first hour, and in the following hours, 4·5—5, 5·3—5·8, 6·0—6·5, and 7·8—9, etc. The stage of development of the eggs during this interval was also noticed. The heat produced in the consumption of 1 mg. oxygen ("caloric quotient" of oxygen respiration) was also determined. This was found in cases of normal fertilisation to be 2·65—2·75. This same quotient was also determined under various conditions of artificial membrane formation. The results obtained are discussed in some detail by the author. S. B. S.

The Lipoids of Egg-Yolk. CESARE SERONO and ANTOINETTO PALOZZI (*Chem. Zentr.*, 1911, ii, 772; from *Arch. farm. sperim.*, 1911, 11, 553—570).—One hundred grams of fresh yolk yield 14—17% egg oil, 11—12% lecithin, and 4% lutein. The last two were extracted with alcohol, and the first-named by extracting the alcoholic residue with ether. The residue after extraction with alcohol and ether was free from fatty acids. The egg-oil has a yellow colour, and smells like olive oil; it solidifies at 15°; it is neutral, and does not show absorption bands or optical activity, and does not contain cholesterol. Various constants (iodine number, etc.) are similar to those of olive oil. It is easily saponified. It contains 68·68% triolein and 30·04% tripalmitin. Lutein and lecithin were separated by acetone, in which reagent the lecithin is insoluble. The lecithin yielded palmitic and oleic acids and choline. Lutein crystallises out from acetone in fine needles and plates, and in large, fluorescent lamellæ. In the air it is rapidly oxidised by an oxydase in the yolk, and became reddish-yellow in colour. It is saponifiable with difficulty, and on decomposition yields free cholesterol and free fatty acids (cholesterol 39%, oleic acid 34%, and palmitic acid 9%). Lutein is regarded as an ethereal combination of cholesterol and fatty acids; glycerol was not detected. A synthetically prepared ester of similar composition was more resistant than lutein and less soluble in alcohol. W. D. H.

The Chemistry and Energy Dissipation in Sleeping Children. JOHN HOWLAND (*Zeitsch. physiol. Chem.*, 1911, 74, 1—12).—A calorimeter of the Benedict-Atwater type was used for observations on three children, three to seven months of age. Details are given of the diet, excretions, heat production, etc., in each, and these results are compared with those obtained from ill-nourished or feeble children. The law that heat production is proportional to the surface area of the body is true only for those who are well nourished. W. D. H.

Choline in Ox-Brain. MAX KAUFFMANN (*Zeitsch. physiol. Chem.*, 1911, 74, 175—178).—Gulewitsch felt doubtful whether the small amount of choline he obtained from ox-brain was free, or, more

probably, a decomposition product. If hydrolysis of lecithin or other phosphatide is prevented by the avoidance of hydrolytic agents, no free choline is discoverable. W. D. H.

Cholesterol Obtained from the Skull Contents of an Egyptian Mummy. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, **74**, 392—393).—The brain-pan of an Egyptian mummy contained a brown, wax-like mass, from which a number of crystals had separated. These are identified as cholesterol. E. F. A.

The Function of the Choroid Glands and its Relation to the Toxicity of Cerebro spinal Fluid. S. P. KRAMER (*Brain*, 1911, **34**, 39—44).—A normal saline extract of the choroid gland (choroid plexuses) injected into an anæsthetised animal intravenously causes a temporary fall of arterial pressure; no effect on the heart beat is noticeable. A similar effect obtained by the intravenous injection of certain specimens of cerebro-spinal fluid from pathological cases is attributed to excess of the choroid secretion. W. D. H.

Swelling Capacity of Nerve Tissue. JULIUS BAUER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 112—116).—The influence of the addition of small quantities of hydrochloric, nitric, sulphuric, lactic, acetic, and boric acids to water on the swelling capacity of nerve tissue has been investigated. The data show that the swelling of nerve tissue of rabbits and cats is diminished by all six acids if the concentration is greater than 0·0005*N*. Similarly, the swelling of human brain tissue is decreased in all cases if the concentration of the acid is greater than 0·001*N*. These results show that acids have a dehydrating effect on the swelling of nerve tissue, as has been already found in the case of lipoids. Fischer's theory, according to which œdema is due to the increased swelling of tissue consequent on the formation of acid substances, cannot therefore be accepted in so far as brain and nerve tissue are concerned.

Salts diminish the swelling capacity of human brain tissue, and a similar influence is found in the case of non-electrolytes. In the case of very dilute acid solutions, the swelling is sometimes greater, sometimes less, than for pure water. H. M. D.

Fat Removal in Peripheral Nerve-degeneration. W. KELMAN MACDONALD (*J. Path. Bact.*, 1911, **16**, 71—74).—Nerve-degeneration was produced in rabbits by cutting the sciatic. The nerves were examined by the Marchi method. Six days after the operation, the fatty débris had not been carried beyond the confines of perineurium; five days later it had reached the septa between the nerve bundles. A few days later the amount inside the perineural sheaths was greatly lessened. Phagocytic and scavenger cells are the main agents in the transport. W. D. H.

Qualitative Analysis of Tissue Lipoids. J. LORRAIN SMITH and W. MAIR (*J. Path. Bact.*, 1911, **16**, 131—134).—The material is

fixed by formaldehyde, and methods are described for estimating the acidity of the chloroformic extract, the total alkali used in saponification, the cerebrosides, the cholesterol both free and combined as esters, and phosphorus to indicate the amount of phosphatide. The method of saponification used (barium hydroxide) completely saponifies fat and lecithin, but leaves the cerebroside almost untouched. Contrasting the brain of the child and adult, it was proved that phosphatides are more abundant, and cholesterol and cerebroside less, in the child. In cases of hemiplegic softening, the cholesterol, especially that in ester form, is increased, but the cerebroside and the phosphorus are reduced. In cases of general paralysis, cholesterol is normal in amount, but cerebroside and, to a less extent, the phosphorus are reduced.

W. D. H.

The Influence of Lecithin on Absorption by the Skin. S. Borschim (*Biochem. Zeitsch.*, 1911, 35, 471—477.—The hair was partly removed from rabbits, and the influence of lecithin in various preparations on the absorption of potassium iodide, eserine sulphate, tetanotoxin, and other substances, when rubbed into the hairless skin, was investigated, the urine being examined for these substances. Lecithin appears to promote very slightly the absorption of potassium iodide, but had no effect on the resorption of the other substances. The author used in a modified form Paolini's method for estimating colorimetrically the iodine in urine.

S. B. S.

The Significance of Oxygen for the Growth of Mammalian Tissue. Leo Loeb and Moyer S. Fleischer (*Biochem. Zeitsch.*, 1911, 36, 98—113).—The experiments were carried out by transplanting tissues to an artificial medium of blood-plasma, which was afterwards allowed to clot. The influence of oxygen on the formation of new tissue in this artificial medium was investigated.

A certain oxygen tension is necessary for growth under these conditions. In the complete absence of oxygen, the tissue dies, and it loses not only its capacity for growth, but also its phagocytic capacity. If the amount of oxygen ordinarily available is diminished, as, for example, by covering the tissue with the plasma coagulum, the growth of the cells and the number of surviving cells are diminished. Normal growths and carcinomata behave similarly, and no marked difference could be noticed between epithelial and connective tissue; the latter appears, however, to be somewhat more resistant when deprived of oxygen. Increase of oxygen tension in the atmosphere surrounding the plasma coagulum generally increases the peripheral surface of living tissue and also the processes of growth (mitoses).

S. B. S.

Creatine and Creatinine. II. Inanition and the Creatine Content of Muscle. Lafayette B. Mendel and William C. Rose (*J. Biol. Chem.*, 1911, 10, 255—264).—In the rabbit and fowl in inanition, an increase occurs in the percentage of creatine in their muscles, and there is no reasonable ground for doubting the origin of urinary creatine and creatinine in endogenous metabolism. Contrary

results reported by Howe and Hawk in the dog are severely criticised. The increase may be due (1) to a removal of the non-creatine portion of the muscle, or (2) to an increased formation of creatine. Reasons are given why the first is probably the correct view to take.

W. D. H.

Antipneumin. Fr. Batelli and Mlle. Lina Stern (*Biochem. Zeitsch.*, 1911, 36, 114—143. Compare this vol., ii, 748).—Antipneumin is the substance which exists in many tissues, and has the capacity of diminishing primary respiration. It is precipitated with the nucleoprotein when an aqueous extract of the tissues is acidified with acetic acid (1 in 1500), and if the precipitate thus obtained is dried, a powder can be obtained containing antipneumin, which retains its specific action for a long period. Muscles and heart contain little, if any, antipneumin; the spleen is the richest in this substance. It is destroyed by heating to 65°, by moderate concentrations of acid and alkali, and by treatment with alcohol and acetone. It is not destroyed by peptic digestion, and is not dialysable. It is carried down generally with precipitates. It does not digest fibrin. Its action is inhibited by blood and by phosphates, and in investigating the content of any tissue in antipneumin, care must be taken to take into account the amount of phosphates present. Its inhibitory action on pnein is not immediate, but can only be detected after it has acted for some time. If tissue is allowed to remain in contact with an antipneumin solution and then washed, its respiratory capacity is not inhibited, and the antipneumin action appears therefore, at any rate after a short contact, to be reversible. There is no evidence that pnein and antipneumin are directly antagonistic. The action of the latter on primary respiration affects both the oxygen consumption and carbon dioxide output, so that there is little effect on the respiratory quotient. It has no action on the accessory respiratory processes (on the alcohol oxydase, urico-oxydase, or the oxidation of succinic acid). It inhibits the oxidation by the tissues, on the other hand, of citric acid (a primary oxidative process). It appears to regulate chiefly the post-mortal oxidative processes.

S. B. S.

The Magnitude of the Work of the Liver. Otto Porges (*Biochem. Zeitsch.*, 1911, 36, 342—343).—In reference to Verzár's paper with this title (this vol., ii, 746), the author claims that his own experiments (Abstr., 1910, ii, 785), carried out with a different technique, are of value in arriving at conclusions as to changes of respiratory quotient produced by throwing the liver out of general circulation.

S. B. S.

Inversion of Sucrose by Bees. A. Korndoerfer (*Chem. Zentr.*, 1911, ii, 777; from *Apoth. Zeit.*, 1911, 28, 659).—Two bees were transferred in the autumn to an empty honey-comb and fed with a 50% solution of sucrose. After half an hour, the sugar transferred to the comb was removed; it retained 42—44% of invert sugar. A single passage of the sugar solution through the honey sack of the bee suffices to invert 80% or more.

E. F. A.

Peptolytic Enzymes in Parasitic Worms. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, **74**, 409—410).—Unless working under strictly comparable conditions the yield of tyrosine from silk-peptone is only a rough measure of the amount of peptolytic enzyme present. The intestinal contents of various intestinal worms gave wholly negative results by this and by the optical method. But if the worms were chopped up, the extracts showed the presence of peptolytic enzymes in large amounts, and the biggest yield was obtained from the intestinal walls of such worms. W. D. H.

The Shield of Chelone Imbricata. HANS BUCHTALA (*Zeitsch. physiol. Chem.*, 1911, **74**, 212—220).—Investigation of various epidermal horny appendages has shown great differences in their composition. The horny plate of the tortoise was subjected to hydrolysis and estimation of amino-acids with the following results. Glycine, 19·36; alanine, 2·95; valine, 5·23; leucine, 3·26; phenylalanine, 1·08; tyrosine, 13·59; cystine, 5·19, and glutamic acid, 0%. The high percentage of glycine and of tyrosine, the low percentage of leucine and cystine, and the absence of glutamic acid are remarkable. Of the total nitrogen, 94·84% is in the form of mono-amino-acids, 0·02% as melanin, 3·04% as ammonia, and 3·09% as diamino-acids. W. D. H.

Experimental Glycosuria. VII. The Amount of Glycogenase in the Liver and in the Hepatic Blood as Affected by Stimulation of the Splanchnic Nerve. JOHN J. R. MACLEOD and R. G. PEARCE (*Amer. J. Physiol.*, 1911, **28**, 403—421).—Stimulation of the great splanchnic nerve of the dog increases the reducing power of the blood issuing from the liver, but no increase in the glycogenolytic power of the liver-extracts. The blood issuing from the liver possesses the same glycogenolytic power before and during stimulation of the nerve. The conclusion is drawn that modifications in the glycogenolytic activity of the liver do not depend on changes in the amount of glycogenase, but on changes in the conditions under which a constant amount of this enzyme is acting. W. D. H.

Isolation of the Individual Acids in Bile. FRITZ PREGL and HANS BUCHTALA (*Zeitsch. Physiol. Chem.*, 1911, **74**, 198—211).—The crude acids obtained by boiling ox bile with sodium hydroxide for twenty-four hours and then acidifying have been separated from each other by a modification of Langheld's process (Abstr., 1908, ii, 211). The results in the main confirm those of Langheld, the acids being obtained in the following percentages (calculated on the quantity, 674 grams, of the dry, crude acids): fatty acids, 10·8; cholic acid, 51·2; deoxycholic acid, 13·5; choleic acid, 11·9; uncrystallised acids, 12·6. Contrary to the previous experience of the authors and of Langheld, it was found that, with this particular bile, sodium cholate did not crystallise from the boiling alcoholic solution.

In the course of the research it became evident that the presence of the fatty acids prevents the isolation of the specific bile acids by

any short process. However, by the following method, 50—70% of the specific bile acids can be obtained in a crystalline state directly from the aqueous solution of the bile after it has been boiled with sodium hydroxide (3·75 mols.) for twenty-four hours. The aqueous alkaline solution (after one extraction with ether to remove the cholesterol, if desired) is treated with ether, acetic acid (3 mols.) is added, and then hydrochloric acid (3·75 mols.) under stated conditions. The crystalline mass which separates consists essentially of cholic, choleic, deoxycholic, and a small quantity of the higher fatty acids, whilst the aqueous solution contains the greater portion of the fatty acids and of the deoxycholic acid. The crystalline mass is digested with alcohol, and is thus separated into a sparingly soluble residue containing cholic and choleic acids, and an alcoholic solution of deoxycholic and the fatty acids. The separation of the constituents of the several fractions does not present any difficulty.

Of the two preceding methods, the former is the more certain and more generally applicable; human bile has been examined by both processes, without success by the latter method, whilst by the former the crude acids have been almost entirely separated into the individual crystalline constituents. C. S.

Compounds of the Aromatic Series as Cholagogues M. PETROWA (*Zeitsch. physiol. Chem.*, 1911, **74**, 429—435).—Sodium benzoate and salicylate, thymol, phenol, guaiacol, and menthol all cause a great increase in the secretion of bile, and all of them are excreted as ethereal sulphate. Thiocol (potassium *o*-guaiacolsulphonate) has no such action; it is itself an aromatic sulphonate, and therefore the liver can effect no further union with sulphuric acid. W. D. H.

The Bile of the Hippopotamus. OLOF HAMMARSTEN (*Zeitsch. physiol. Chem.*, 1911, **74**, 123—141).—Hippopotamus bile does not give the ordinary reactions for bile pigment; when freed from mucus it has a reddish-green colour. It contains two pigments, which give absorption spectra like that of cholehæmatin (found also in sheep and ox-bile). It contains 10·9% of salts soluble in water, but insoluble in alcohol; these are mainly chlorides; carbonates come next, with a small amount of sulphates and traces of phosphates. Of the material soluble in alcohol, 95·4% is precipitable by ether. It is poor in phosphatides, but contains a substance similar to jecorin. Cholesterol is absent, and the material soluble in ether, which is very scanty, is olein with a little solid fat. The bile is rich in glycocholic acid, and contains also taurocholates; about 6·4% of the sulphur is in ethereal sulphates. The cholic acid from the taurocholate is the usual kind; the glycocholic fraction yields a little cholic acid, but this is not quite certain; its chief acid is one not hitherto found, although it resembles hyocholic acid in some points; it contains 1·2% of sulphur. W. D. H.

Colostral Fat. ST. ENGEL and A. BODE (*Zeitsch. physiol. Chem.*, 1911, **74**, 169—174).—The colostrum of cows has been collected immediately after calving, on the following day, and also at subsequent

intervals. The fat has been extracted and examined for the iodine number and also for the saponification number, Reichert-Meissl value, and Polenske value by Arnold's method. In agreement with previous observations, it is found that the iodine number, initially about 43, decreases as the period of lactation increases. The saponification number varies considerably (217·9—226·4 on the second day) in fats from different cows, but increases as the lactation period increases. The Reichert-Meissl value increases considerably (from 23·4 to 30·2) between the first and second day, then increases more slowly, and after about a week sinks to the normal value, 29·0. The Polenske value increases with the period of lactation, attaining the value for milk fat after the first week.

According to the preceding constants, the colostral fat of a cow distinctly shows the characteristics of a milk fat, but less pronouncedly. The transition of the colostral fat into milk fat is gradual, only the Reichert-Meissl values showing a marked increase from the first to the second day. The colostral and the milk fats exhibit slighter differences in the case of a goat than of a cow. C. S.

Influence of Sodium Chloride on the Excretion of Bromides. CESARE PADERI (*Chem. Zentr.*, 1911, i, 1867; from *Arch. farm. sperim.*, 1911, 11, 196—213).—Dogs on a normal diet of cooked horse-flesh received 5 to 10 grams of sodium chloride and 2·5 to 5 grams of potassium bromide; the giving of the bromide increased the excretion of sodium chloride in the urine, and the elimination of bromide was increased by the administration of chloride. If the diet was free from chlorides, bromism was more readily induced than in normal animals, and bromides accumulated in the blood. The explanation is based on osmotic phenomena. W. D. H.

The Amount of Alcohol Excreted by the Animal Organism under Various Conditions. II. Influence of Muscular Work on the Excretion of Alcohol in Expired Air and Urine. WILHELM VÖLTZ and AUGUST BAUDREXEL (*Pflüger's Archiv*, 1911, **142**, 47—88. Compare this vol., ii, 218).—A continuation of previous researches on the same subject. The factor specially investigated was the influence of muscular work; this increases the frequency of respiration, and it is this that leads to a greater amount of alcohol finding its way into the expired air than during repose. There is also a considerable increase in the amount of the ingested alcohol which leaves the body by the urine, although it still remains less than the amount expired. Full numerical details are given. W. D. H.

Free Amino-acids in the Intestinal Contents of Certain Mammals. EMIL ABDERHALDEN (*Zeitsch. physiol. Chem.*, 1911, **74**, 436—444).—About one-fifth of the total nitrogen in the intestinal contents of dogs, pigs, oxen, and horses is contained in the form of free amino-acids. A few estimations are given of those which can be estimated by simple crystallisation; the ester method lead to great loss. In the case of dogs, the intestinal contents from 100 dogs were collected together; the estimation of amino-acid nitrogen works

out at about 0·1 gram per dog. The material has to be boiled to prevent further enzymic cleavage of polypeptides. W. D. H.

Creatine and Creatinine. III. Excretion of Creatine in Infancy and Childhood. WILLIAM C. ROSE (*J. Biol. Chem.*, 1911, 10, 265—270).—Creatinine excretion in young children is very low. The muscles of a new-born infant contain more creatine than embryonic muscles, but less than adult muscle. This coincides with Mellanby's statement that age is an important factor. It will account for the low creatinine excretion in infants, and furnishes further evidence for the origin of urinary creatinine in muscle metabolism. Creatine is usually present in the urine until the age of puberty. It is conceivable that the demand for carbohydrates by growing tissues is so great that the cells are left in partial carbohydrate hunger, and are thus unable to perform the "endo-katabolic" activities as perfectly as in later life. W. D. H.

Studies on Water-Drinking. IV. The Excretion of Chlorides when Large Amounts of Water are taken between Meals. S. A. RULON, jun., and PHILIP B. HAWK (*Chem. Zentr.*, 1911, i, 1867; from *Arch. intern. Med.*, 7, 536—550).—The investigations were performed on healthy young men in nitrogenous equilibrium. In two cases the urinary chloride increased on the day the water was taken, and then returned to normal; this is explained on the supposition that the secretion of gastric juice was increased, and the excess of hydrochloric acid was absorbed and excreted as ammonium chloride; the water would also stimulate protein katabolism in the tissues. In one case the increase of chlorides in the urine occurred on the day after the excess of water was taken; here it is considered that the diluted blood would seek to recoup its chlorides from the tissues, and that with the fall in intake of water, these would be excreted. W. D. H.

Fasting Studies. IV. (Studies on Water-Drinking. VII.) Allantoin and Purine Excretion of Fasting Dogs. S. R. WREATH and PHILIP B. HAWK (*J. Amer. Chem. Soc.*, 1911, 33, 1601—1622).—A study has been made of the allantoin-nitrogen and purine-nitrogen excretion of three adult dogs which were subjected to fasts of from forty-eight to ninety-six days and of a pup which was subjected to a seven-days' fast. The data obtained for the allantoin-nitrogen excretion show considerable variations, which appear to be functions of the age and development of the animals. A decreased excretion of purine-nitrogen was observed in all cases. The effect of a large increase in the ingestion of water during the fast produced a marked increase in the output of allantoin-nitrogen and a much more pronounced decrease in that of the purine-nitrogen. The sum of the allantoin- and purine-nitrogen excreted was higher during the four days in which large quantities of water were ingested than during any other four-day period of the fast, and this indicates that the water stimulated protein katabolism. E. G.

The Excretion of Quinine by the Dog, and a New Method for the Estimation of this Alkaloid. JULIUS KATZ (*Biochem. Zeitsch.*, 1911, **36**, 144—189).—In quinine salts the acid can be estimated quantitatively by titration with alcoholic potassium hydroxide solution, using Poirrier's blue as indicator. This method can also be applied to estimation of other cinchona alkaloids. If an alcoholic solution of quinine is evaporated with hydrochloric acid on a water-bath in presence of sodium chloride, the salt

$$C_{20}H_{24}O_2N_2,2HCl$$

can be obtained free from excess of hydrochloric acid and the mono-acid salt. To obtain quinine from urine, the latter is treated with half its weight of ammonium sulphate and extracted with a mixture of 1 part of chloroform and 3 parts of ether. The extract can be cleared with magnesia usta.

The dog excretes in the urine smaller amounts of quinine than does the human subject; only a small part remains unabsorbed in the fæces. The quinine excretion ceases the fourth day after ingestion. The amount excreted is less when the quinine is administered subcutaneously, and still less when given intramuscularly, than after ingestion *per os*. After administration of aristochin, the excretion (of quinine) is at first smaller than after quinine, but with continued administration, increases; the excretion also continues for a much longer period after the ingestion of the drug has ceased. Subcutaneous and intramuscular injections of quinine cause vomiting. S. B. S.

The Iron in the Urine of Domestic Animals. MAX REICH (*Biochem. Zeitsch.*, 1911, **36**, 209—239).—The estimation was carried out by means of a slightly modified Neumann method. The normal urines were found to contain on an average 1 mg. iron per kilo., somewhat about the same amount as is found in human urine. There was not much difference in the iron content whether the animals were fed on an iron-rich or iron-poor diet in the cases of dog, pig, and sheep. The iron is present as an inorganic ferric compound in the colloidal state, and can be precipitated from the urine by calcium chloride. S. B. S.

Purine Metabolism in Diseases of the Liver. S. LA FRANCA (*Biochem. Zeitsch.*, 1911, **35**, 434—444).—Patients with liver cirrhosis were fed on diets free from purines, or containing known amounts of purines (or caffeine), and the amounts of uric acid and purine nitrogen excreted in the urine were determined under these two conditions. It was found in Laennec's atrophic cirrhosis, that the purine destruction in the body was defective, whereas in Hanot's hypertrophic cirrhosis the purine destruction was more or less normal. S. B. S.

Auto-intoxication and Nephritis in Rabbits. W. HENWOOD HARVEY (*J. Path. Bact.*, 1911, **16**, 95—104).—That products of protein decomposition (*p*-hydroxyphenylethylamine and the like) when formed in excess in the alimentary canal and absorbed may be factors in the production of renal disease is confirmed by the present experiments on rabbits. Nephritis was produced in the majority of the animals

dosed with such substances, either given by the mouth or intravenously injected over considerable periods. Many also developed degenerative changes in the aorta.
W. D. H.

The Action of Cholesterol Derivatives with Lecithin in the Syphilis Reaction. CARL H. BROWNING and J. CRUICKSHANK (*J. Path. Bact.*, 1911, **16**, 135—136).—The addition of cholesterol to lecithin increases the amount of complement absorbed in the presence of syphilitic serum. A large number of cholesterol derivatives were investigated, but none was found equal to cholesterol itself.
W. D. H.

Pharmacological Behaviour of Certain Insoluble Preparations of Mercury. I. EDUARDO FILIPPI (*Arch. farm. sperim.*, 1911, **11**, 457—474; Reprint).—The action of mercury compounds ($HgCl$, HgI, HgI_2, HgO, and mercury salicylate) was studied by digesting them with various organs *in vitro*, at 38°; fifteen hours later, after filtration and centrifugalising, the organic substance was destroyed and the mercury estimated electrolytically; the amount of mercury per 100 grams of organ (liver, spleen, muscle, kidney, etc.) varied between 0·02 and 0·2. Mercury sulphide does not go into solution. The mercury which is dissolved from the other compounds is in part dialysable and precipitable by hydrogen sulphide, in part dissolved in a colloidal state, and in part firmly united to organic substances. The latter compounds increase in amount with more lengthy (eight days) digestion at the cost of the other portions.
W. D. H.

The Influence of Potassium Iodide on the Accumulation of Mercury in the Liver. FERDINAND BLUMENTHAL and KURT OPPENHEIM (*Biochem. Zeitsch.*, 1911, **36**, 291—300).—Mercury was estimated by Salkowski's method, the tissues being partly destroyed by potassium chlorate and hydrochloric acid. From an aqueous extract of the residue the mercury was deposited on copper, from which it was expelled by heating in a test-tube. The condensed metal was rendered visible by converting it into the iodide with iodine vapour. The experiments were carried out on rats and rabbits with a variety of mercury compounds (nitromercuribenzoate, diamino-mercuribenzoate, mercuric chloride, asurol, etc.). It was found that the liver was the only organ in which the mercury was constantly found. It was also observed that the rate of excretion after subcutaneous injection of compounds easily soluble in water was not always more rapid than in the case of those compounds which are only slightly soluble. If potassium iodide is administered simultaneously with the mercury compounds, the deposition of mercury in the liver was inhibited.
S. B. S.

The Behaviour of Ethylene Glycol, Propylene Glycol and Glycerol in the Animal Body. SOICHIRO MIURA (*Biochem. Zeitsch.*, 1911, **36**, 25—31).—When glycerol or ethylene glycol is given to animals either by the mouth or subcutaneously, no derivatives of

glycuronic acid or other reducing substances are found in the urine. Propylene glycol, on the other hand, is excreted as a derivative of glycuronic acid, which may be isolated from the urine as barium propyleneglycolmonoglycuronate. W. J. Y.

The Action of Intravenous Injections of Concentrated Solutions of Sugar and Salt. G. G. WILENKO (*Arch. exp. Path. Pharm.*, 1911, **66**, 143—159).—Intravenous injection of concentrated salt solution in rabbits causes hyperglycæmia by stimulation of the central nervous system. The nerve stimulus is the cation. Another effect is first an increased and then a lessened permeability of the kidneys for sugar. This is determined by osmotic factors. The effect of concentrated solutions of dextrose on the kidney is the same, but less well marked. W. D. H.

The Behaviour of *o*-Iodoanisole in the Organism. RICCARDO LUZZATO and G. SATTA (*Arch. farm. sperim.*, 1911, **11**, 393—404; Reprint).—Doses of 5—6 grams of *o*-iodoanisole in dogs cause local excitation, but no toxic effects. It is excreted in part unchanged in the fæces; about 40% appears in the urine; a small fraction of the iodine is there in inorganic union; the greater part is present as ethereal derivatives, probably as esters of *o*-iodoquinol monomethyl ether (35% being present as sulphate and 65% as glycuronate).
W. D. H.

The Behaviour of Iodo-fat Derivatives of Cholesterol in the Dog's Body. EMIL ABDERHALDEN and EMIL GRESSEL (*Zeitsch. physiol. Chem.*, 1911, **74**, 472—480).—*α-Iodopropionylcholesterol* crystallises in tufts of needles, m. p. 115°; *β-iodopropionylcholesterol* crystallises in plates, m. p. 100°; *di-iodoelaidylcholesterol*, m. p. 90°, was not obtained in crystalline form. All three are badly absorbed, two-thirds of the iodine given being recovered in the fæces. Iodine passes into the urine for four or five days after the administration, and a considerable fraction of what is absorbed remains in the tissues. W. D. H.

Behaviour of Some Aliphatic Iodo-acids in the Organism. GIACOMO PONZIO (*Gazzetta*, 1911, **41**, i, 781—787. Compare Abstr., 1904, i, 548; 1905, i, 405).—In view of the use of calcium iodobehenate as a drug, the author has investigated the physiological action of some salts and amides of aliphatic iodo-acids formerly prepared by him. *Calcium α-iodopalmitate*, $Ca(C_{16}H_{30}O_2I)_2$, is an amorphous powder. *α-Iodopalmitamide*, $C_{16}H_{32}ONI$, is prepared: (1) from ammonia and 2-iodopalmityl chloride (obtained with phosphorus pentachloride); (2) from α-bromopalmitamide by heating it for some hours with an alcoholic solution of potassium iodide. The substance crystallises in large, lustrous laminæ, m. p. 108°. *α-Bromopalmitamide* crystallises in small, colourless plates, m. p. 85°.

Calcium α-iodostearate, $Ca(C_{18}H_{34}O_2I)_2$, is an amorphous powder. *α-Iodostearamide*, $C_{18}H_{36}ONI$, crystallises in large, lustrous laminæ, m. p. 112°. *α-Bromostearamide*, $C_{18}H_{36}ONBr$, crystallises in small, colourless plates, m. p. 91°.

The administration of the calcium salts is well supported by the organism, and they are absorbed, the iodine being liberated in the urine, but the amides pass through the gastrointestinal canal for the most part unchanged. R. V. S.

The Behaviour of Stereoisomeric Tartaric Acids in the Dog's Organism. CARL NEUBERG and SUMIO SANEYOSHI (*Biochem. Zeitsch.*, 1911, **36**, 32—36).—When dogs were fed with either *d*- or *l*-tartaric acid, the same percentage of the total acid reappeared unchanged in the urine, whilst when racemic acid was given, the acid found in the urine was still optically inactive. There is thus no evidence that *l*-tartaric acid is used up in the body more quickly than *d*-tartaric acid (compare Brion, Abstr., 1898, ii, 618). W. J. Y.

The Method of Action of Phenylcinchonic Acid on the Purine Metabolism of the Dog. KONRAD FROMHERZ (*Biochem. Zeitsch.*, 1911, **35**, 494—502).—The influence of the administration of atophan (phenylcinchonic acid) on the allantoin, uric and phosphoric acid excretions of dogs in different circumstances of nutrition was investigated. Somewhat varying effects were obtained. The author believes that the most probable action of the drug is the increase of the capacity of the kidneys for excreting the degradation products of nucleic acid. When this capacity has already reached its maximum, the action of the drug would naturally have no effect. S. B. S.

The Influence of Saponin on the Physiological Action of Digitoxin. J. J. POSTOÉEFF (*Biochem. Zeitsch.*, 1911, **36**, 335—341). —The investigation was undertaken with the object of determining whether saponins increase the toxic action of digitoxin, Straub's method of perfusion through the frog's heart being employed. To produce the death of the heart, within a half hour, it was found that doses of 0·025 mg. and upwards were necessary. If 0·02 mg. saponin be present in the Ringer's solution (2 c.c.), then a dose of only 0·02 mg. digitoxin was capable of producing death (cession of ventricular beat) within this period. S. B. S.

The Action of Crystalline Aconitine on the Isolated Frog's Heart. CURT HARTUNG (*Arch. exp. Path. Pharm.*, 1911, **66**, 1—57).—A detailed experimental study of the action of aconitine on the frog's heart. The effect is a depressant one, first the ventricular and then the auricular beats being extinguished. The heart-muscle is paralysed. W. D. H.

The Action of Crystalline Aconitine on the Motor Nerve and Skeletal Muscles of Cold-blooded Animals. CURT HARTUNG (*Arch. exp. Path. Pharm.*, 1911, **66**, 58—70).—The effect of aconitine on nerves is first stimulating (unless the solution is very dilute), then paralysing. The question whether the drug acts also on the motor endings of the nerve in muscle is discussed. W. D. H.

Adrenaline Immunity. N. WATERMAN (*Zeitsch. physiol. Chem.*, 1911, **74**, 273—281).—Various explanations of the so-called adrenaline immunity are discussed, such as a change in the substance in the

myoneural junction on which adrenaline acts, a paralysis of the autonomic nervous system, and the relationship between adrenaline administration and an increase of the blood-sugar. No very definite conclusion is reached. W. D. H.

Influence of Caffeine on the Ureopoëtic System of the Liver. GIOVANNI BATTISTA ZANDA (*Chem. Zentr.*, 1911, i, 1602; from *Arch. farm. sperim.*, 11, 125—135).—Diuretin and caffeine increase the sugar and urea in the blood, and the urea in the liver. This increase may explain the diuretic power of these drugs.
W. D. H.

The Influence of Substances of the Digitalin Group on Blood-pressure in the Rabbit. HERNANDO (*Arch. exp. Path. Pharm.*, 1911, 66, 118—131).—The rise of pressure produced by strophanthin and helleborein is variable, but is especially small in chloralised animals. If the pressure is first lowered by bleeding, the rise is more pronounced. The effect is mainly of cardiac origin, and chloral lessens the excitability of cardiac muscle. W. D. H.

The Action of Morphine, Codeine, Dionine, and Heroine, on Breathing. B. VON ISSEKUTZ (*Pflüger's Archiv*, 1911, 142, 255—272).—From experiments on rabbits, the conclusion is drawn that there is no qualitative difference in the action of the four drugs mentioned in the title on respiration. All of them lessen the number of inspirations, also their volume and energy, if the animal to start with is breathing normally. If, however, the breathing is superficial, these drugs increase the volume and the energy of the respiratory act. W. D. H.

The Influence of Tetrahydro-β-naphthylamine on Temperature and Respiratory Exchange. N. MUTCH and MARCUS S. PEMBREY (*J. Physiol.*, 1911, 43, 109—129).—This compound causes rapid respiration, convulsions, excitation of sympathetic nerves, and other symptoms which may end fatally. Particular attention was paid to the rise of temperature which occurs, and is due to increase of muscular action produced by action on the central nervous system. This is antagonised by anæsthetics. W. D. H.

Action of β-Iminazolylethylamine [4-β-Aminoethylglyoxaline]. HENRY H. DALE and PATRICK P. LAIDLAW (*J. Physiol.*, 1911, 43, 182—195).—This compound produces a vaso-dilator fall of blood pressure in carnivora, monkey, and fowl. This is a direct effect of the base. It slightly retards blood coagulation, accelerates the flow of lymph in the thoracic duct, and lowers body temperature.
W. D. H.

Biochemical Investigation of Aromatic Mercury Compounds. FERDINAND BLUMENTHAL (*Biochem. Zeitsch.*, 1911, 35, 503—505. Compare this vol., ii, 577).—A reply to Schrauth and Schoeller (this vol., ii, 687). S. B. S.

The Mechanism of Antagonistic Salt Action. JACQUES LOEB (*Biochem. Zeitsch.*, 1911, 36, 275—279).—The author recapitulates several of his recently published results on the toxic action of sodium chloride on marine organisms, all of which show that the toxic action ceases to exist when potassium chloride and calcium chloride are present in the same relative proportions as they exist in blood and sea-water. He gives reasons for showing that this combination of salts is no mere nutrient medium, but ascribes their combined action to their effect on the colloids. The three salts in the proper relative proportions so act on the colloids (of the egg membrane, etc.) that these have just the correct permeability for salts and other substances which is necessary for the maintenance of the correct vital conditions. As the proteins alter in presence of different cations and anions (Pauli) as regards their physical character, the salts being quantitatively different in their actions in this respect, no other combinations can be substituted for the combination of the chlorides of sodium, potassium, and calcium as they exist in sea-water. S. B. S.

Nerve Excitability in Oxalate Poisoning. RICHARD CHIARI and ALFRED FRÖHLICH (*Arch. exp. Path. Pharm.*, 1911, 66, 110—117). —The excitability of the vagus to faradic stimulation is lowered, and its susceptibility to atropine is increased, in oxalate poisoning. Calcium chloride in cases of slight poisoning by oxalates antagonises these effects. The excitability of autonomic nerves is affected in the same way, although the movements of the small intestine are unaffected. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Optional Forms of Lactic Acid Produced by Pure Cultures of Bacillus Bulgaricus. JAMES N. CURRIE (*J. Biol. Chem.*, 1911, 10, 201—211).—Various strains of this bacillus from different sources in pure cultures produce different varieties of lactic acid. The *d*-lactic acid strain predominates. In some cases inactive lactic acid is formed, which probably necessitates the presence of both dextro- and lævo-acid-producing enzymes in the same organism. The bacilli of *B. Bulgaricus* type in human fæces and human saliva are identical. Some strains produce small amounts of succinic acid which may account for the presence of this acid in Cheddar cheese. W. D. H.

The Influence of Strychnine on Bacteria. WL. S. SADIKOFF (*Centr. Bakt. Par.*, 1911, i, 60, 417—425).—Experiments showed that certain bacteria were able to grow in bouillon to which had been added 0·2—5·0% of strychnine phosphate, sulphate or chloride. The organisms were found to be more sensitive when grown on strychnine agar, but *Proteus*, *Bacillus subtilis*, *B. mesentericus*, *B. coli*, and *B. typh*

were able to grow in the presence of 0·5% of the phosphate. *Staphylococcus aureus* and some moulds were more resistant; the former organism becomes non-chromogenic when strychnine chloride is used instead of the phosphate. In like manner, the secretion of tryptase, invertase, and maltase is checked, or the enzymes are destroyed.

The non-toxic behaviour of these salts is believed to be due to the deposition of free strychnine by ammonia and basic amides formed in the cultures. H. B. H.

Action of Gypsum on Nitrification. SERAFINO DEZANI (*Chem. Zentr.*, 1911, ii, 157; from *Staz. sper. agrar. ital.*, 1911, **44**, 119—137).—Soil (1—2 grams) with magnesium carbonate (2 grams), a solution of an ammonium salt (200 c.c.), and gypsum (0·5 to 2·0%), both with and without organic matter, was inoculated with *B. Nitrosomonas* and with *B. Nitromonas* respectively, and the ammonia, nitrites, and nitrates estimated from time to time. Similar experiments were made with an artificial soil and with soil (500 grams). Nitrification was not materially increased by the presence of gypsum.

N. H. J. M.

Sugar Tests and Pathogenicity in the Differentiation of Streptococci. J. M. BEATTIE and A. G. YATES (*J. Path. Bact.*, 1911, **16**, 137—138).—Forty-two strains were investigated. Gordon's tests do not differentiate those which are pathogenic and those which are not. W. D. H.

Fixation of Nitrogen by Yeasts and other Fungi. CHARLES B. LIPMAN (*J. Biol. Chem.*, 1911, **10**, 169—182).—Eighteen organisms, yeasts, pseudo-yeasts, and moulds were found to show a more or less pronounced power of fixing atmospheric nitrogen. The highest amount fixed was 2·94 mg. per gram of mannitol by pseudo-yeast Tulare No. 46b in solution of mannitol in distilled water. *Aspergillus niger* and *Penicillium glaucum* fix nitrogen as stated by previous observers. *Botrytis cinerea*, a parasitic fungus, has the same power. W. D. H.

Fermentations with Yeast in Absence of Sugar. III. CARL NEUBERG and LÁSZLÓ KARCZAG (*Biochem. Zeitsch.*, 1911, **36**, 60—68).—In earlier communications (this vol., ii, 320, 520) it was shown that a number of substances other than sugars give off carbon dioxide when treated with yeast.

In the cases of pyruvic, *d*-tartaric, and glycerophosphoric acids, it is now found that this evolution of carbon dioxide in presence of yeast is accompanied by a considerable disappearance of the substance. The other products of the fermentation have also been isolated in the cases of pyruvic and oxalacetic acid (next abstract).

The carbon dioxide is therefore due to a true fermentation of the substance, and not to an increase in the auto-fermentation of the yeast, as was obtained by Harden and Paine (Proc., 1911, **27**, 103) by the addition to yeast of a molar solution of sodium chloride or ammonium sulphate. On the other hand, the authors were only able

to repeat the results obtained by Harden and Paine on rare occasions, neutral salts, as a rule, producing on the contrary an inhibition of the auto-fermentation. This difference in behaviour is ascribed to the difference between English and German yeasts. W. J. Y.

Fermentations with Yeast in Absence of Sugar. IV. A New Enzyme in Yeast-Carboxylase. CARL NEUBERG and LÁSZLÓ KARCZAG (*Biochem. Zeitsch.*, 1911, 36, 68—75).—Free pyruvic acid and oxalacetic acid in solutions of 1% are fermented by yeast with production of carbon dioxide and acetaldehyde: $CH_3\cdot CO\cdot CO_2H = CO_2 + CH_3\cdot CHO$; $CO_2H\cdot CH_2\cdot CO\cdot CO_2H = 2CO_2 + CH_3\cdot CHO$. The acetaldehyde may be detected by distilling the mixture and isolating from the distillate by means of the *p*-nitrophenylhydrazone. These decompositions are not brought about when yeast which has previously been heated is employed, but are found to occur with yeasts which have been killed with acetone, toluene, etc. It is therefore due to an enzyme to which the name *carboxylase* is given.

When potassium pyruvate is fermented, the reaction goes somewhat differently, potassium carbonate being formed: $2CH_3\cdot CO\cdot CO_2K + H_2O = 2CH_3\cdot CHO + CO_2 + K_2CO_3$. In this case some of the carbon dioxide will be held in solution, forming potassium hydrogen carbonate, and the aldehyde will be polymerised in presence of alkali. The fermentation of potassium pyruvate is therefore more difficult to demonstrate. W. J. Y.

Fermentations with Yeast in Absence of Sugar. V. Carboxylase. CARL NEUBERG and LÁSZLÓ KARCZAG (*Biochem. Zeitsch.*, 1911, 36, 76—81).—This enzyme was found to be present in all the different races of yeast tried; almost all yeasts fermented pyruvic acid, whilst all fermented oxalacetic acid. The action of the enzyme may readily be demonstrated by incubating at 38°, 12 c.c. of a 1% solution of the acid with 2 grams of yeast in a Schrötter's fermentation tube. After twenty to twenty-five minutes a quantity of carbon dioxide will have collected, and the liquid in the tube will smell of acetaldehyde, the presence of which may be confirmed by its *p*-nitrophenylhydrazone.

The enzyme is distinct from zymase. W. J. Y.

The Theory of Disinfection. REGINALD O. HERZOG and R. BETZEL (*Zeitsch. physiol. Chem.*, 1911, 74, 221—241).—Various antiseptics (chloroform, mercuric chloride, phenol, etc.) were investigated, and yeast was the organism selected for experiment. Adsorption plays a part in the process, and this is reversible; it follows the logarithmic law. This is the first phase in disinfection; the second is the chemical action of the disinfectant on the micro-organism; the law for this part of the action is not a simple one, as determined by counting the dead cells, and requires further investigation. W. D. H.

Inhibiting Action and Germ-destroying Power of Free Sulphurous Acid, its Salts, and other Complex Derivatives. EBERHARD HAILER (*Arb. Kais Gesundheits-Amt*, 1911, 36, 297—340). —An account of comparative tests with solutions of various concentrations on moulds, yeasts, and bacteria. The experiments are divided into two classes, the "static" series, in which the nutritive mixtures containing the organism were allowed to remain under the influence of varying concentrations of the respective inhibiting reagents, and the "kinetic" series, in which the organism was submitted for a certain time to the inhibiting reagent, a culture then transferred to the nutritive broth, and the presence or absence of life demonstrated. The resistance of the organism to the concentration of the disinfectant, as a rule, followed the order, that if the concentration of the germicide sufficient to kill the very sensitive bacteria be taken as unity, then yeast would require four times, and moulds five times, that concentration for their destruction.

The compounds employed were sulphuric and sulphurous acids, sodium and sodium hydrogen sulphites, and the sodium sulphite compounds of acetone, formaldehyde, acetaldehyde, and dextrose respectively, their action being compared with each other and with phenol.

F. M. G. M.

The Respiration of Plants. W. ZALESKI and A. REINHARD (*Biochem. Zeitsch.*, 1911, 35, 228—245).—The destruction of the structure of the cells (by grinding in a mortar) causes in some plants an increased and in others a diminished respiration. The disintegration of the killed material, in contrast to the results obtained with the living material, has either no influence on the respiratory energy, as measured by the carbon dioxide output, or increases it. When the plants are killed, the anaerobic processes become more prominent; the more important the rôle played by such processes in the living plant, the less is the respiratory process of the plant interfered with when it is killed. The effects of various substances on the respiratory energy were also investigated. It was found that sugar solutions which had been fermented with zymin, and to a greater extent neutralised extracts of the corresponding quantity of zymin, or expressed yeast juice, stimulate the respiratory energy of pea and wheat seeds. Quinine has no effect on the respiration of sprouting pea seeds.

S. B. S.

The Nutrition of Green Plants with Formaldehyde and Formaldehyde-yielding Substances. THOMAS BOKORNY (*Biochem. Zeitsch.*, 1911, 36, 83—97).—Stronger solutions of formaldehyde are toxic to plants. From dilute solutions, however (0·001%), spirogyra, which has been rendered starch-free by keeping in the dark and treatment with calcium nitrate, can synthesise starch. Cress, also, which has been rendered starch-free, can form starch if kept under a bell-jar over sodium hydroxide solution to which has been added not too much formaldehyde (0·1%). With methylal, plants remained alive, but did not form starch until they were exposed to light. Algæ can form starch from the sodium bisulphite compound of formaldehyde if

disodium or dipotassium phosphate is present, which renders the sodium sulphite set free harmless. With flowering plants, on the other hand, no definite positive result was obtained when this substance was used. Methyl alcohol stimulates the growth of pea-seedlings. S. B. S.

Amounts of Substances Yielding Hydrogen Cyanide in Some Fruit Seeds. PAUL HUBER (*Landw. Versuchs.-Stat.*, 1911, 75, 462—482).—Native pear seeds contain no amygdalin, or not more than 0·0025%. Apple seeds were found to contain approximately the amounts of amygdalin found by Lehmann (0·46—1·21%). The seeds of sweet apples generally contain less hydrogen cyanide than those of sour apples. Seeds of apple and pear quinces cannot be distinguished by the amounts of amygdalin they contain.

Seeds of stone fruits contain considerably more hydrogen cyanide-producing substances than hitherto supposed. As much as 0·3% of hydrogen cyanide was obtained in some cases, corresponding with 5% of amygdalin.

No relation seems to exist between the amount of total nitrogen in the seeds and the amount of glucosides producing hydrogen cyanide. N. H. J. M.

Phytase in Lower Fungi. ARTHUR W. DOX and ROSS GOLDEN (*J. Biol. Chem.*, 1911, 10, 183—186).—An enzyme which decomposes phytin into inositol and phosphoric acid was first noted in rice bran by Suzuki and his colleagues. It is probable that such an enzyme is present in all plants which contain phytin, or at any rate has a wide distribution. It has not been found in animal tissues; the present research shows that it occurs in various kinds of *Aspergillus*; the enzyme is present there in both the intra- and extra-cellular form. W. D. H.

The Inulinase of Aspergillus niger. J. BOSELLI (*Ann. Inst. Pasteur*, 1911, 25, 695).—The secretion of inulinase by *Aspergillus* is the same whether inulin, sucrose, dextrose, lævulose, or sucrose and peptone are employed. The enzyme diffuses with ease into the culture liquid, especially when the culture is old.

The optimum acidity for the activity of the enzyme varies with the acid used and inversely with the temperature; at 51° the optimum concentration of sulphuric acid is $N/200$, and that of acetic acid $N/12·5$. At a given temperature the amount of change corresponds with the concentration of acid, optimum concentrations of acetic and sulphuric acids leading to equal changes. Slight alkalinity arrests the action of inulinase. The rate of change conforms to the logarithmic law. H. B. H.

Micro-chemistry of Plants. I. The Micro-chemistry of Birch Camphor. O. TUNMANN (*Chem. Zentr.*, 1911, i, 1656; from *Apoth. Zeit.*, 1911, 26, 344—345).—When small, thin lamellæ of birch-bark are submitted to sublimation, the birch-camphor (betuline) is obtained as a crystalline sublimate; these crystals consist of long,

fine prisms or needles, which are grouped together in masses. They are soluble in aniline, slightly soluble in aqueous chloral hydrate solution, acetic acid, and benzene, and insoluble in water, alcohol, light petroleum, carbon disulphide, chloroform, and ether. The crystals yield a yellow coloration when treated with sulphuric acid. The quantity of birch-camphor in birch-bark may be estimated by the micro-sublimation process, and tables are given showing percentages of camphor for different lamellæ. W. P. S.

Soluble Carbohydrate of Chestnut Flour. GIOVANNI LEONCINI (*Chem. Zentr.*, 1911, i, 1873; from *Staz. sperim. agrar. ital.*, 44, 113—118).—The flour is extracted with water and a little lead acetate, and the filtrate polarised; about 26% of sucrose is present. Erythro-, amylo-, and acro-dextrin are absent. These are perhaps formed when the temperature at which the chestnuts are roasted is too high.

E. F. A.

Colour Changes Occurring in the Blue Flowers of the Wild Chicory, Cichorium intybus. JOSEPH H. KASTLE and R. L. HADEN (*Amer. Chem. J.*, 1911, 46, 315—325).—The flowers of the blue variety of the wild chicory, *Cichorium intybus*, are blue when they first open, but in the course of a few hours undergo a remarkable series of changes, first becoming pink, then white, and, finally, brown. The present investigation was undertaken in order to ascertain the causes of this phenomenon.

It has been found that the colour changes are partly due to variations in the amount of acid contained in the pigment-cells and partly to the action of an oxydase occurring in the flower which oxidises and destroys the pigment. It is shown that the decomposition of the pigment can also be brought about by the oxydase of the potato as well as by various other oxidising agents, such as potassium ferricyanide and permanganate, *p*-benzoquinone, and hydrogen peroxide.

The flowers of the white variety of the wild chicory rapidly wither and turn brown, and in this case also an oxydase is present.

E. G.

Occurrence of Fraxin in Diervilla lutea. CHARAUX (*J. Pharm. Chim.*, 1911, [vii], 4, 248—250).—The stalks and roots of the shrub *Diervilla lutea* (*D. Canadensis*) contain a glucoside which the author has identified as fraxin, a substance separated originally from *Fraxinus excelsior* and later from *Fraxinus ornus*, etc. A substance similar to saponin was also present. W. P. S.

Micro-Chemistry of Plants. II. Detection and Localisation of Andromedotoxin in Ericaceæ. O. TUNMANN (*Chem. Zentr.*, 1911, ii, 644; from *Apoth. Zeit.*, 1911, 26, 555—556).—Thin sections of parts of the plant are shaken with water for ten minutes and then treated with concentrated hydrochloric acid; in the presence of andromedotoxin, a greenish-blue coloration is produced, which changes gradually to violet-red. With 25% phosphoric acid solution a violet-

red coloration is also produced, and this coloration is still more intense when phosphoric anhydride is used. The compound is present in almost all parts of the leaves, the outer parts of the stalks, and capsules, and buds of *Ericaceae*; it has a powerful toxic action.

W. P. S.

The Green and the Yellow Colouring Matters of the Florideæ. HARALD KYLIN (*Zeitsch. physiol. Chem.*, 1911, 74, 105—122).—As a contribution to the solution of the vexed question whether the green colouring matter extracted from florideæ by alcohol is identical or not with the chlorophyll of higher plants, the author finds that the colouring matter from *Ceramium rubrum* contains magnesium (compare Willstätter and Isler, this vol., i, 392).

With regard to the yellow colouring matters in the florideæ, the author has isolated from *Ceramium rubrum* three substances; one of these is carotin, another is xanthophyll (probably identical with the xanthophyll of higher plants), whilst the third (fucoxanthin ?), which presents a great similarity to xanthophyll, but differs from it in its solubility in petroleum, is probably derived, not from the *Ceramium rubrum* itself, but from the diatomaceæ and fucoids with which it is unavoidably contaminated.

C. S.

Composition of the Fat from the Seeds of Lophira Alata. SAMUEL S. PICKLES and WILLIAM P. HAYWORTH (*Analyst*, 1911, 36, 493—494).—The fatty acids separated from this fat consisted of 50% of saturated acids comprising arachidic acid, m. p. 77·5°, palmitic acid, m. p. 62·5°, and a small quantity of another acid, and 50% of unsaturated acids consisting of about equal quantities of oleic acid and linoleic acid.

W. P. S.

Composition of Para Rubber-seed Oil. SAMUEL S. PICKLES and WILLIAM P. HAYWORTH (*Analyst*, 1911, 36, 491—492).—The composition of the mixed fatty acids obtained from a sample of Para rubber-seed oil was found to be: saturated (solid) acids, 14%, consisting of stearic acid, m. p., 69°, and an acid or mixture of acids, m. p. 56·5°; unsaturated (liquid) acids consisting of oleic acid, 32·6%, linoleic acid, 50·9%, and linolenic acid, 2·5%.

W. P. S.

Composition of Pear and Apple Seeds. PAUL HUBER (*Landw. Versuchs-Stat.*, 1911, 75, 443—461).—The dried seeds of two varieties of pears (1 and 2) and of apples (3) were found to have the following percentage composition:

	Fat.	Sugar.	Furfuroids.	Crude fibre.	N as protein.	N as bases.	Ash.	P as phosphatides.	P as lecithin.
1.	24·84	5·13	6·72	10·90	4·961	0·205	3·83	0·048	1·23
2.	25·15	5·62	6·72	7·15	5·921	0·216	4·19	0·032	0·82
3.	24·03	3·42	6·66	8·96	4·87	—	3·79	0·038	0·99

The composition of the separated germs and husks is also given in each case.

N. H. J. M.

Localisation and Distribution of the Essential Oil in "Bupleurum fruticosum" (Linn.). LUIGI FRANCESCONI and E. SERNAGIOTTO (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 111—117).—The essential oil is present in the form of minute drops in the epidermis of the leaves, and in the cells immediately beneath it, and is abundant in certain small vessels which terminate there. Young leaves contain much more than older ones. In the vessels of the stem, and in its epidermis (especially when young), the essential oil is present in considerable quantity, and is particularly evident in regions where growth is taking place. The root also contains it, but not in great amount. The oil is also present in the seed, to which it gives a strong, aromatic odour. R. V. S.

Oil and Cholesterols of the Soy Bean. HERMANN MATTHES and A. DAHLE (*Arch. Pharm.*, 1911, 249, 424—435).—See this vol., i, 831, 858.

The Relation of Certain Non-leguminous Plants to the Nitrate Content of Soils. T. LYTTLETON LYON and JAMES A. BIZZELL (*J. Franklin Inst.*, 1911, 171, 1—16, 205—220).—An account of numerous experiments intended to illustrate the relationship between soil, temperature, and nitrification, both in the presence and absence of growing crops. The results are tabulated, and the following facts deduced:

That the nitrate content of soil under timothy, corn, potatoes, oats, millet, and Soy beans was different for each crop when on the same soil.

There was a characteristic relationship between the crop and the nitrate content of the soil at different stages of growth.

During the most active growing period of the corn crop, nitrates were higher under corn than in cultivated soil bearing no crop; under a mixture of corn and millet at this period, the nitrates were higher than under millet alone, although the crop yields were about the same in each case.

Both under corn and oats the nitrate content was higher during the period when the crop was making its greatest draft on the soil nitrogen than in the later stages of growth; nitrates under these crops and under millet failed to increase late in the season when nitrogen absorption had practically ceased, although uncropped soil showed a very large increase in nitrates at that time; this fact is accounted for on the supposition that plants in later periods of growth exert a retarding influence on nitrification.

Changes in the moisture content, or in the temperature of soil under crops during the growing season, did not materially affect the nitrate content except under the legume soy beans, but on uncropped soil an increased moisture content during September was accompanied by a marked increase in nitrates. F. M. G. M.

Analytical Chemistry.

Estimation of Moisture in Various Substances by means of Magnesium Methyl Iodide. TH. ZEREWITINOFF (*Zeitsch. anal. Chem.*, 1911, **50**, 680—691).—The process is briefly as follows. The substance (coal, starch, etc.) is treated with anhydrous pyridine and a solution of magnesium-methyl iodide in amyl ether is added. The operation is carried out in a kind of a Lunge nitrometer, which is fully described and figured in the original paper. The moisture, being rapidly absorbed by the pyridine, is at once acted on by the reagent, and the methane evolved, which represents the water, is then measured with the usual precautions. L. DE K.

Modified Cobalt Reaction for the Detection of Small Quantities of Hydrogen Peroxide. M. LEUCHTER (*Chem. Zeit.*, 1911, **35**, 1111).—To a 1% solution of crystallised cobaltous chloride is added an equal volume of a solution of 1·6 parts of borax, 20 parts of glycerol (D 1·24), and 100 parts of water. One to two c.c. of the mixture are placed in a very narrow test-tube, and an equal volume of the liquid to be tested is carefully poured over the surface. If hydrogen peroxide is present, a brownish-black ring is formed at the place of contact, and if much is present, a decided evolution of gas will be noticed.

The above reaction is also given by perborates, but not by persulphates. On warming, however, these also give the reaction. Addition of a few drops of sodium hydroxide solution also promotes the reaction sometimes. L. DE K.

Estimation of Fluorine [in Silicates]. M. KLEINSTÜCK (*Zeitsch. anal. Chem.*, 1911, **50**, 697).—A solution of zinc oxide in ammonium carbonate is recommended for the removal of the last traces of silica from the alkaline solution. L. DE K.

New Apparatus for the Estimation of Sulphur and Carbon in Iron and Steel. D. A. WENNMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 1861—1862. Compare this vol., ii, 938).—*Estimation of Sulphur.* —In the estimation of sulphur the material is often dissolved in concentrated acid, which necessitates the passage of the gases evolved through water. The author finds that it is not necessary to have a continuous stream of cooling water, and has therefore devised a special cooler for the gases, which is fitted into the decomposition flask by a ground-glass joint, the whole apparatus being made of glass. Everything is so arranged that the gases evolved from the flask have to pass through water contained in the cooler before escaping to the absorption vessels. There are also the necessary tubes for running the acid into the flask, and for passing a current of carbon dioxide through the apparatus towards the end of the estimation. A diagram is given of the apparatus, which is very compact.

Estimation of Carbon.—A condenser is fitted into the decomposition flask by a ground-glass joint, a special tube being sealed through the bottom of the condenser for leading gases free from carbon dioxide through the apparatus. A diagram is given. T. S. P.

Estimation of Sulphuric Acid in Soils. P. DE SORNAY (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **29**, 133—136).—The soil (10 grams), with 1 gram of potassium nitrate and 5 c.c. of water, is dried on a sand-bath, ignited, treated with 25 c.c. of hydrochloric acid, and evaporated on a sand-bath until all the silica is rendered insoluble. It is then treated with 20 c.c. of hydrochloric acid and 5 c.c. of water, heated for thirty to forty-five minutes on a sand-bath, filtered, and washed with about 100 c.c. of water. Barium chloride is then added, and the estimation completed in the usual manner. N. H. J. M.

Rapid Estimation of Nitrogen. OSWALD CLAASSEN (*Chem. Zeit.*, 1911, **35**, 1130—1131).—Three grams of the dried and thoroughly powdered and mixed sample are heated in a Kjeldahl flask with 20 c.c. of sulphuric acid, 5 grams of potassium sulphate, and eight drops of mercury. Heat is applied first to the sides of the flask for ten minutes, after which the flask is placed in the usual position. The operation is finished within twenty to thirty minutes. In order to hasten the cooling, a small lump of ice may be introduced.

The soda solution used for the titration may be checked as follows. The ammonia evolved by boiling 1 gram of ammonium chloride with aqueous sodium hydroxide is collected in standard sulphuric acid, and the excess of acid is then titrated back. If the acid itself requires 146·1 c.c. of soda solution, and after the operation only 39·6 c.c., 106·5 c.c. of soda solution have been used up, corresponding with 0·262038 gram of nitrogen; 1 c.c. therefore equals 0·00245844 gram. L. DE K.

Apparatus for the Estimation of Nitrogen by Kjeldahl's Method. KRIEGER (*Chem. Zeit.*, 1911, **35**, 1063).—In order to avoid loss of ammonia during neutralisation, and bumping during distillation, the flask is provided with a tap-funnel, through which the alkali is introduced, the stem of the funnel having a branch through which steam may be passed.

A simpler method is to employ a large flask, of 500 c.c. capacity for 20 c.c. of sulphuric acid, and add a little mercury. After cooling, 250 c.c. of water are added, followed by 10 c.c. of 4% potassium sulphide and 50 c.c. of concentrated sodium hydroxide solution. Neutralisation and distillation are completed without loss of ammonia. C. H. D.

Analysis of Lime Salpetre, "Kalk Stickstoff," and "Stickstoff Kalk." E. DINSLAGE (*Chem. Zeit.*, 1911, **35**, 1045—1046).—*Lime Salpetre.*—The analysis (including the estimation of any nitrite) is conducted like that of an ordinary crude nitre. The moisture, however, cannot be readily estimated in the ordinary way, but may be determined within twenty minutes by heating 3—5 grams

of the sample in a porcelain crucible over a small flame some 10 cm. distant from the crucible. Care must be taken that the mass does not melt.

"*Kalk Stickstoff.*"—The usual Kjeldahl process gives unsatisfactory nitrogen figures, but the following modification gives trustworthy results. One gram of the sample is boiled in a flask with 30 c.c. of a mixture of equal vols. of sulphuric acid and water, with addition of a few drops of mercury. The conversion into ammonia is complete in at most two hours; addition of potassium sulphate towards the last is superfluous. The ammonia is then distilled off as usual. The estimation of the various mineral constituents and pre-existing ammonia is carried out by the usual analytical methods.

"*Stickstoff Kalk.*"—The same process as for "Kalk Stickstoff" is recommended. This product is distinguished from the former by its dark colour and tarry odour, and by its chlorine content.

L. de K.

Estimation of Phosphoric Acid by Direct Weighing of Ammonium Phosphomolybdate. Norbert von Lorenz (*Oesterr. Chem. Zeit.*, 1911, 14, 1—5. Compare Abstr., 1908, ii, 777, 895, 983).—Experimental details of methods previously advocated for the direct estimation of phosphoric acid as ammonium phosphomolybdate in soils, manures, and vegetable ash are discussed. A detailed account is given of the author's method of preparing the required reagents, the amount of material to employ, and the modifications recommended in the respective cases of various soils, soluble phosphatic manures, basic slag, superphosphates, and bone meal. F. M. G. M.

Estimation of Arsenic in Pyrites. Georg Hattensaur (*Oesterr. Zeitsch. Berg. & Huttenwesen*, 1911, 59, 175—178).—The author discusses Vilstrup's method for the analysis of pyrites (Abstr., 1910, ii, 458), and recommends that the arsenious sulphide be redissolved in hydrochloric (or hydrobromic) acid treated with bromine and subsequently heated to remove excess, the solution rendered ammoniacal, and the arsenic reprecipitated as magnesium ammonium arsenate; this is collected after twenty-four hours, redissolved, and estimated by any of the known methods, or the redissolved sulphide may be evaporated with nitric acid until free from chloride, the arsenic precipitated as silver arsenate, collected, ignited, and the metallic silver weighed. F. M. G. M.

Detection of Small Quantities of Arsenic in Urine, Blood, and Other Organic Substances. Georg Lockemann (*Biochem. Zeitsch.*, 1911, 35, 478—493).—The following processes are described: (1) The destruction of organic matter: for which fuming nitric acid and a mixture of potassium and sodium nitrates are employed. (2) The precipitation of the arsenic: which is brought about by adding ferric ammonium sulphate to the solution and precipitating therefrom ferric hydroxide by the quantitatively correct amount of ammonia solution. (3) The detection of arsenic in this precipitate by a

specially constructed Marsh apparatus. The last traces of arsenic are removed from the reagents by the ferric hydroxide method, the full experimental details of which are given in the paper. S. B. S.

Estimation of Carbon in Irons and Steels in the Electric Furnace. HANS AUGUSTIN (*Zeitsch. angew. Chem.*, 1911, **24**, 1800—1803).—The process recommended is essentially the same as the one described by Lorenz (Abstr., 1893, ii, 491). The sprinkling over the iron with lead chromate cannot be recommended, but the use of copper oxide in the front part of the porcelain combustion tube is absolutely necessary to ensure complete oxidation of the carbon.

An electric furnace is described and figured, whereby it is possible to heat the iron at 1000° and the copper oxide layer at 800°. The combustion is carried out in a current of purified oxygen, and after passing through drying tubes containing sulphuric acid, the carbon dioxide is absorbed in the usual soda-lime tubes. L. DE K.

Analysis of Graphite. FRIEDRICH MAYER (*Chem. Zeit.*, 1911, **35**, 1024—1025).—The amount of carbon present in graphite may be estimated by taking the calorific value of the substance. In order to ensure the complete combustion of the graphitic carbon, 0·6 gram of the graphite is mixed with 0·4 gram of pure benzoic acid, and the calorific value of the mixture is determined in a Berthelot's bomb. One kilo. of graphitic carbon yields 7900 Cal., and 1 kilo. of benzoic acid, 6322 Cal. If the graphite under examination contains sulphur, an allowance must be made for its quantity. For this purpose, the sulphuric acid formed during the combustion is estimated by titrating the solution of the acid in the water contained in the bomb; for each c.c. of $N/10$ solution required for the titration, 7·06 Cal. are deducted from the result first obtained. W. P. S.

Detection of Carbon Monoxide by means of Blood. HARTWIG FRANZEN and O. VON MAYER (*Zeitsch. anal. Chem.*, 1911, **50**, 669—697).—The gas to be tested is shaken with blood (preferably ox-blood), which is then examined for carbon monoxide by one of the usual methods. The original Hoppe-Seyler sodium hydroxide process cannot be recommended, but the Salkowski modification of the same readily detects 1% of carbon monoxide in the blood. Salkowski's hydrogen sulphide method and Rubner's tannin process are less delicate, only showing 5% or above. The Kunkel and Welzel ferrocyanide method and their original tannin process are also capable of indicating as little as 1% of carbon monoxide. The full details of these processes, with some comments by the authors, are recapitulated in the original article. L. DE K.

Microchemical Analysis of Silicates. RICHARD CANAVAL (*Zeitsch. prakt. Geol.*, 1910, **18**, 460—461).—A process by which the constituents of refractory minerals can be qualitatively determined. The finely powdered substance is thoroughly mixed with an equal volume of lead oxide, and carefully fused in small portions to a globule on an aluminium spoon; the cooled pulverised globule is then frequently

evaporated with nitric acid, after which the silica, lead, and other constituents can be separated or identified by various processes described in the original. F. M. G. M.

Detection of Silicates, Fluorides, and Silicofluorides. Philip E. Browning (*Amer. J. Sci.*, 1911, [iv], **32**, 249—250).—A small lead cup about 1 cm. in diameter and depth is made by running the melted metal into a mould, and a flat piece of lead with a small hole in the centre is used as a cover. Into this cup is placed about 0·1 gram of powdered calcium fluoride, together with 0·1 gram or less of the silicate, and the mixture is carefully moistened with a few drops of sulphuric acid. Upon the upper side of the cover is placed a piece of moistened black paper, and upon this a small moistened pad of ordinary filter paper, so as to keep the black paper moist during the ten minutes' heating on a steam-bath. At the conclusion of the experiment a white deposit is found on the underside of the black paper over the opening in the cover if silica was present in appreciable amount. Conversely, the process may be used for the detection of fluorides by heating these with silica and sulphuric acid; silicofluorides are decomposed by sulphuric acid readily in the cold. L. de K.

Qualitative Analysis of Metals without Employment of Hydrogen Sulphide or Ammonium Sulphide. G. P. Pamfil (*Mon. Sci.*, 1910, [iv], **24**, II, 641—644).—The mixed metals are evaporated several times with nitric acid, whereby stannic oxide and antimony tetroxide are separated.

Silver chloride, mercurous chloride, and lead chloride are precipitated with hydrochloric acid; after boiling with ammonium chloride, bismuth oxychloride separates; the filtrate is rendered alkaline with potassium hydroxide, and ammonia eliminated by boiling; the solution is again cleared by boiling with hydrochloric acid, after which the addition of potassium hydroxide and hydrogen peroxide precipitates the oxides and hydroxides of manganese, cobalt, nickel, copper, mercury, iron, titanium, zirconium, uranium, and part of the magnesium; the solution is then acidified with hydrochloric acid and saturated with ammonia, when aluminium phosphate and hydroxide separate.

The solution is acidified, and on subsequent treatment with ammonium carbonate yields barium, strontium, and calcium carbonates, and when again acidified, followed by the addition of potassium ferrocyanide, furnishes zinc hydroxide; the further addition of hydrogen peroxide and ether precipitates the chromium, leaving only the arsenic and remainder of the magnesium, which are finally precipitated with excess of ammonium hydroxide. The further separation of the individual elements is carried out by known methods.

The presence of iron being found to vitiate the hydrogen peroxide test for titanium, the author recommends the employment of potassium persulphate in dilute sulphuric acid solution, accompanied by a control containing the equivalent colorimetrically in ferric sulphate to which hydrogen peroxide and a standard solution of a titanium solution can be added for comparison. F. M. G. M.

A Method of Qualitative Analysis. D. A. ROCHE (*Mon. Sci.*, ill. [v], 1, I, 87. Compare preceding abstract).—An adverse iticism of Pamfil's method of analysing metals without the employ-ent of hydrogen sulphide or ammonium sulphide; the author states at the possibility of other insoluble residues besides stannic oxide d antimony tetroxide remaining after treatment with nitric acid is t considered, and suggests the presence of silica, titanium oxide iO_2), and possibly barium sulphate; also, that the separation of lead not complete, that the silver would be liable to be overlooked, and at phosphoric acid would be precipitated before the stage indicated Pamfil. F. M. G. M.

Potassium: its Detection as the Cobaltinitrite. LEON BOWSER (*J. Amer. Chem. Soc.*, 1911, 33, 1566—1569).—The sitiveness of the author's method for detecting potassium as the altinitrite (Abstr., 1910, ii, 346) can be greatly increased by rying out the test in the following manner. Two tall beakers, of —100 c.c. capacity, are placed side by side on a mirror. In one ker are placed 5 c.c. of the solution to be tested, and in the other, c.c. of water, and to each are added 2·5 c.c. of the sodium cobalti-rite reagent and 5 c.c. of 95% alcohol. If, on looking down ough the solutions into the mirror, the image of the observer ears equally sharp in each case, potassium is not present, but the image is dimmed by the liquid in the beaker containing the ution under examination, potassium is present to the extent of or more parts per million. Care must be taken to ensure the ence of ammonia, since ammonium salts are readily precipitated by reagent, 10 parts per million being sufficient to yield a visible udiness. It is also of importance that the solution should be either itral or slightly acidified with acetic acid. E. G.

New Indicator for the Estimation of Alkalis in Blood. CL BERNHARDT (*Chem. Zentr.*, 1911, i, 1763; from *Wien. klin. ch.*, 1911, 24, 606—607).—An indicator, consisting of a mixture 2 volumes of 1% "alizarinsulphazid" solution and 1 volume of 1% igo-carmine solution, is recommended for use in the estimation of alis in blood according to Engel's method (titration with $N/75$-taric acid solution); the indicator exhibits a dark green colour acid solution, and reddish-violet in alkaline solution. W. P. S.

Estimation of Calcium and Magnesium in Hard Water. STHER NOTHNAGEL (*Veroffentlichungen aus dem Gebiete des Militar-itatswesens.*, Heft 45; *Arbb. Hyg.-chem. Untersuchungsstellen*, 1911, Tl. 76—85. Compare Grittner, Abstr., 1902, ii, 696).—A iew of the work of Winkler and Grittner, with numerous tables onstrating the results obtained by various modifications in the eriments carried out by these and other workers.

F. M. G. M.

Estimation of Very Small Amounts of Calcium by means Potassium Permanganate. LEON T. BOWSER (*J. Ind. Engin. m.*, 1911, 3, 82—84).—The solution (5—10 c.c.) containing a

minimum of 0·3 mg. of calcium is treated with a few drops of ammonium hydroxide and about 0·4 gram of ammonium chloride, boiled, and 0·2 gram of ammonium oxalate added, again boiled, and diluted with about its own volume of a 3% solution of ammonium hydroxide and allowed to remain several hours.

The precipitate is collected by suction on an asbestos pad in a tube of "Shimer" form, washed with 3% ammonium hydroxide, and the pad with adherent precipitate transferred to a beaker and treated with 1 c.c. dilute sulphuric acid (50%), titrated in boiling solution with excess of $N/200$-potassium permanganate, and the excess titrated back with $N/200$-oxalic acid. The amount of potassium permanganate consumed by the asbestos, water, and acid must be determined by blank experiments; the first titration of the asbestos oxidises all the impurities, and a second one should be made for the amount to be deducted in the future employment of that pad; one pad suffices for about twelve experiments. Special burettes graduated in 0·1 and 0·01 c.c. are employed, with the ends drawn out so that 10 drops are equivalent to 0·15 c.c. of the solution. The $N/200$-solution of permanganate is not oxidised as much as it should be by theory; therefore it must be standardised against a calcium oxalate solution of approximately the same concentration as that employed in the estimation.

F. M. G. M.

Detection of Certain Elements which Form Insoluble Sulphates: Barium, Strontium, (Calcium) and Lead. PHILIP E. BROWNING and PHILIP L. BLUMENTHAL (*Amer. J. Sci.*, 1911, [iv], **32**, 246—248).—Ten c.c. of the solution are precipitated with hydrochloric acid, and to the filtrate are added 5 grams of ammonium acetate and an excess of 10% solution of ammonium sulphate. After warming the liquid, the sulphates are collected and washed with a saturated solution of ammonium acetate until free from lead; the filtrate and washings are then kept for further testing. After placing in the filter a little sugar carbon, the paper is rolled up and heated in a covered porcelain crucible to full redness for a few minutes. The fused mass is then heated with 5 c.c. of 50% acetic acid to decompose the sulphides formed. The filtrate is then tested for barium with potassium dichromate, and in the filtrate from the barium chromate the strontium and calcium are reprecipitated by boiling with sodium carbonate. The washed carbonates are re-dissolved in nitric acid, and the liquid is examined spectroscopically; if the amount is not too small, the nitrates may be separated by boiling with amyl alcohol.

L. DE K.

Estimation of Magnesium as Oxide. O. KALLAUNER (*Chem. Zeit.*, 1911, **35**, 1165—1166).—The author confirms the statements of Krause and others that magnesium chloride cannot be readily converted into oxide by simple ignition.

Berzelius's method (evaporation of the magnesium chloride solution with mercuric oxide, and ignition of the residue) gives technically correct results, provided that the operation is several times repeated, for even a double treatment with mercuric oxide gave in one of the author's experiments a residue which still contained chlorine.

L. DE K.

Analysis of Cuprous Iodide. H. BARDT (*Zeitsch. anal. Chem.*, 1911, **50**, 695—696).—Five grams of the sample are repeatedly treated with dilute ammonia by decantation and filtration into a half-litre flask until the filtrate is free from copper. The residue is then treated with nitric acid in case it should still contain any copper.

An aliquot part of the ammoniacal solution is placed in a 500 c.c. electrolytic vessel, 5 grams of tartaric acid are added, and then again so much ammonia that there is an excess of about 1—1·5% present. From this solution, the copper is then separated electrolytically as usual. When completely deposited, the cathode is removed and carefully rinsed. The adhering copper is then dissolved in 30 c.c. of nitric acid, diluted to 500 c.c., and, after adding 5 c.c. of sulphuric acid, the solution is again electrolysed ($N.D._{100}$ — 0·5 ampère), using the same cathode. Similarly, the copper is recovered from the nitric acid solution of the insoluble residue. Any copper present as sulphate may be extracted from the sample with water. To the liquid free from copper are added 20 c.c. of chloroform and then an excess of hydrochloric acid. The iodine liberated in then titrated with $N/10$-thiosulphate. L. DE K.

The Spectroscopic Recognition of Traces of Mercury in Nitrocellulose. Stability in Explosives. JEAN FLORIN (*Zeitsch. ges. Schiess. Sprengstoffwesen* 1911, **6**, 21—22, 63—66).—A detailed description of methods employed to demonstrate spectroscopically the presence of mercury in nitrocellulose. Illustrations of the spectroscope and other apparatus employed, with tabulated results and curves, are given in the original. F. M. G. M.

Time Curves for Cadmium Deposited from Organic Electrolytes. MARY V. DOVER (*J. Amer. Chem. Soc.*, 1911, **33**, 1577—1583).—Holmes and Dover (Abstr., 1910, ii, 1111) have shown that cadmium can be deposited in a satisfactory form from various organic electrolytes when the rotating spiral anode is employed and the current is less than one ampere, but that the character of the deposit varies considerably with the different electrolytes. Experiments have now been made to determine the rate of deposition and the quantity of the metal that can be deposited from each electrolyte in a sufficiently adhesive form to allow of accurate weighing. Curves have been constructed for each electrolyte, the time being plotted as the ordinates and the amounts of cadmium deposited as the abscissæ.

It has been found that the maximum quantity of cadmium which will form an adhesive deposit and the rate of deposition vary greatly with the different electrolytes. The data are recorded for cadmium acetate, formate, and lactate in each of the acetate, formate, and lactate electrolytes. The deposits are finer and more adhesive when the solution is decidedly acid, but if too much acid is used, the last traces of the metal cannot be deposited. E. G.

Estimation of Colloids in Arable Soil. JOSEF KÖNIG, JULIUS HASENBÄUMER, and C. HASSLER (*Landw. Versuchs-Stat.*, 1911, **75**, 377—441).—The amounts of colloids in soils may be estimated by

means of a solution of methyl-violet of such a strength that a distinct colour remains after absorption by the soil. Solutions containing 1, 2, and 3 grams per litre may be employed. Absorption of salts was estimated by means of a $N/50$-solution of tricalcium phosphate.

Potassium is chiefly absorbed by the colloidal clay, and it can be more or less completely liberated by oxidation with hydrogen peroxide or by an electric current. Phosphoric acid, on the other hand, is mainly chemically fixed by the production of insoluble phosphates of calcium, etc. The combination is rendered more complete by the action of heat, and even strong electric currents fail to dissolve the phosphoric acid completely.

A method is described for estimating the readily soluble constituents of soils by means of an electric current. The results, as regards potassium, are approximately the same as those obtained by steaming under pressure and oxidation. Results obtained by the latter method agreed well (in the case of potassium) with the amounts actually assimilated by plants. N. H. J. M.

Estimation of Ferric Oxide in the Presence of Alumina. KRIEGER (*Chem. Zeit.*, 1911, 35, 1054).—The weighed mixed oxides, which need not be powdered, are introduced into an Erlenmeyer flask and boiled gently with a mixture of 25 c.c. of sulphuric acid and 25 c.c. of water. After five to ten minutes the iron oxide has dissolved, as may be noticed from the colour of the undissolved alumina. When cold, another 50 c.c. of water and some zinc are added, and finally the iron is titrated with permanganate as usual. L. DE K.

Gravimetric Estimation of Nickel and Cobalt. L. DEDE (*Chem. Zeit.*, 1911, 35, 1077).—To the solution containing the nickel or cobalt is added a very slight excess of potassium hydroxide solution, and then a solution of potassium persulphate. When the supernatant liquid has become colourless, the precipitate is washed with cold water and then collected on a filter. After ignition the oxide is reduced by heating in a current of hydrogen, and the nickel, or cobalt, is then weighed as metal. Salts of ammonium should be absent. L. DE K.

Rapid Estimation of Nickel in Steel. G. RAULIN (*Mon. Sci.* 1911, [v], 1, i, 84—86).—One gram of a steel containing about 1% nickel is dissolved in 10 c.c. hydrochloric acid diluted with an equal amount of water, boiled with 10 c.c. nitric acid, and treated with 200 c.c. water; ammonium hydroxide is added until the solution becomes red but remains clear, followed by a calculated excess of potassium cyanide, and then by a further quantity of ammonium hydroxide, after which the solution is filtered and made up to a volume of 500 c.c. Half of this is removed, treated with 10 c.c. of ammonium sulphate solution, and five drops of potassium iodide solution, followed by titration with silver nitrate; 0·24% must be subtracted from the nickel found as due to the action of the cyanide. The solutions employed should contain respectively the following weight of each salt in grams to the litre: silver, nitrate 5·788; potassium cyanide

445, accompanied by 0·5 of sodium hydroxide; potassium iodide, 200; and ammonium sulphate, 600. The duration of the operation is about half an hour.

F. M. G. M.

Application of Methyl-orange in the Colorimetric Estimation of Titanium. ANDRÉ GAUTIER (*Rev. gén. Chim. pure appl.*, 1911, 14, 16—17).—The stability of methyl-orange as a colorimetric reagent renders it suitable for employment in the estimation of titanium. The relative concentrations of the titanium and methyl-orange solutions which it is advisable to employ are tabulated in the original.

F. M. G. M.

Assay of Platinum. ALBERT STEINMANN (*J. Suisse Chim. Pharm.*, 1911, No. 32, 33, Reprint 8 pp.).—The usual process of cupellation with silver and lead and separation of the silver from the button obtained by boiling with sulphuric acid is not correct, as platinum, in the circumstances, is far from totally insoluble in the acid. The loss, however, is somewhat compensated by the platinum retaining some lead and silver.

The author has found that by using a slightly diluted acid (100 vols. strong acid, 22 vols. water) and heating at 240°, the solvent action of the acid on platinum is reduced to a minimum. The retention of lead and silver in the button may be prevented by adding a suitable amount of copper before cupellation.

L. DE K.

New Method for the Destruction of Organic Matter by Bromine, Specially Applicable in Toxicology. GEORGES MAGNIN (*J. Pharm. Chim.*, 1911, [viii], 4, 302—306).—The substance to be destroyed is treated with bromine in a long-necked flask, and heated on the water-bath. The process is stated to be more rapid, and to give better results than the methods hitherto employed.

W. O. W.

Estimation of Organic Matters in Waters from Sulphur Springs. MAX DITTRICH (*Zeitsch. anal. Chem.*, 1911, 50, 697—700).—The usual method of permanganate titration cannot be applied to waters containing hydrogen sulphide unless the latter is first removed. The author recommends for this purpose a solution of cadmium sulphate. It is, however, necessary to analyse a sample freshly obtained, otherwise the sulphur is not completely removed, and too much permanganate will be consumed.

L. DE K.

Estimation of Caoutchouc as Tetrabromide; the Decomposition of the Bromide by Nitric Acid. DAVID SPENCE, J. C. GALLETLY, and J. H. SCOTT (*Gummi Zeit.*, 1911, 25, 801—803).—The experimental methods advocated by Korneck and Budde (this vol., ii., 545) for the estimation of bromine in caoutchouc tetrabromide are discussed, and a dozen experiments described which show that different results can be obtained by varying the experimental details; these include the presence or absence of silver nitrate during the decomposition and the employment of excess or otherwise, varying

the concentration of the nitric acid and the temperature at which decomposition is carried out, and replacing sealed tubes by other forms of apparatus. F. M. G. M.

Hübener's Caoutchouc Tetrabromide. GERHARD HÜBENER (*Gummi-Zeit.*, 1911, **25**, 634, 751—752); R. BECKER (*ibid.*, 677—678).—Polemical in reference to Hübener's methods for estimating bromine in caoutchouc tetrabromide. F. M. G. M.

A New Method of Estimating Alcohol Vapour. ARTUR BAUDREXEL (*Woch. Brauerei*, 1911, **28**, 21—23. Compare Abstr., 1906, ii, 584).—A sketch of the apparatus employed, with an account of the method by which the author estimates minute quantities of ethyl alcohol colorimetrically by passing the vapour into a solution of potassium dichromate in sulphuric acid. F. M. G. M.

The Proportion of Dextrose to Lævulose in Certain Preserved Fruits. FAVREL and GARNIER (*J. Pharm. Chim.*, 1911, [vii], **4**, 253—255).—The authors find that apricot pulp, dried apricots, and prunes contain about twice as much dextrose as lævulose, and that, consequently, the detection of an excess of dextrose in preserves made from these fruits does not necessarily indicate that added dextrose is present. W. P. S.

Viscosity of Saccharine Solutions. PH. ORTH (*Bull. Assoc. Chim. Sucr. Dist.*, 1911, **29**, 137—148).—The viscosity of saccharine solutions may be expressed by the following equations:

$$\log.(\log.\eta) = 0{\cdot}069498 - 2 + 0{\cdot}03381935(x + Kn) - 0{\cdot}009818782t$$

and $100K = 156{\cdot}89 - 0{\cdot}81586m + (0{\cdot}0187228m - 1{\cdot}38441)t$,

in which η is the viscosity compared with distilled water at 20° = 1, x the amount of sugar % obtained by inversion (Clerget), n the non-sugar %, m the dry matter, and t the temperature. The equations hold good with percentages of sugar between 60 and 76, with dry matter between 65 and 82%, and at temperatures from 20° to 90°.

Viscosity increases very rapidly with diminished temperature, especially when the concentration is high. N. H. J. M.

Detection of Small Quantities of Disaccharides. CARL NEUBERG and SUMIO SANEYOSHI (*Biochem. Zeitsch.*, 1911, **36**, 44—55).—The method is applicable to those disaccharides which form phenylosazones.

Maltose may be detected in the presence of other disaccharides by converting into the osazones, dissolving in water, and treating with yeast maltase for two days. The maltosazone is converted by the enzyme into glucosazone and dextrose. The solution is filtered and treated with mercuric acetate, and the dextrose estimated in the filtrate by Fehling's solution after removal of the excess of mercury with hydrogen sulphide.

In this way 0·01 gram of maltosazone may be detected. *iso*Maltosazone is not attacked by yeast enzymes, but may be hydrolysed by heating with 1·5% sulphuric acid, when dextrose is set free and may be detected as before. Lactosazone and melibiosazone may be hydrolysed with emulsin or kefirlactase, or by heating with 1·5% sulphuric acid

with formation of galactose and glucosazone. The method allows of the detection of these substances in presence of hexoses and of pentoses, the osazones of which will not be hydrolysed in the above manner. W. J. Y.

The Estimation of Carbohydrates by Oxidation with Permanganate in Alkaline Solution. W. GREIFENHAGEN, JOSEF KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, **35**, 169—193).—All carbohydrates, multivalent alcohols, the corresponding aldehydes and ketones, and polysaccharides are oxidised in alkaline solutions quantitatively to oxalic acid and carbon dioxide. The details of the method for estimating the oxidation products are given by the authors. If the oxidation is carried out with standardised permanganate solution and the reaction mixture is afterwards acidified, then by titration of the excess of permanganate with oxalic acid, the amount of oxygen used in the oxidation process can be determined. The terminal groups of the sugars appear to be oxidised in alkaline solution to carbon dioxide, the intermediate groups yielding oxalic acid. In the case of ethylene glycol and erythrol, the results obtained indicate the formation of polymerides as intermediate products. Formic acid was never detected amongst the oxidation products. S. B. S.

The Estimation of Starch. W. GREIFENHAGEN, JOSEF KÖNIG, and A. SCHOLL (*Biochem. Zeitsch.*, 1911, **35**, 194—216).—The polarimetric method of Lintner's (polarisation after treatment with cold more concentrated hydrochloric acid) and of Ewer's (polarisation after treatment with warm more dilute acid) are applicable to all varieties of starch. The rotatory power by Lintner's process is about the same for all kinds of starch (+202°), whereas that by Ewer's differs for the different starches from maize, rice, wheat, rye, barley, and oats, but has a mean value of about 183°. In applying the method to fodder, etc., it is advisable to treat the material first with water, alcohol, and ether to remove other substances which effect the polarisation. Cellulose, hemicellulose, and pentosans have no effect in these processes. Condiments and foodstuffs can also be examined by the methods; in certain cases (for example, cinnamon) the material should be treated with hot alcohol before submitting it to either process. The conclusion is drawn that these processes are as valuable for examination of foodstuffs as the ordinary gravimetric methods. S. B. S.

Estimation of Volatile Acids in Wine. A. VERDA (*Chem. Zentr.*, 1911, ii, 643; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 340—341).—The usual method of estimating the volatile acids in wine (titration of 200 c.c. of distillate obtained by distilling 50 c.c. of the wine with steam) appears to yield low results in the case of wines from Southern Italy; it is recommended, therefore, that the distillation be continued until the distillate no longer exhibits an acid reaction when tested with litmus paper, showing that the whole of the lactic acid present has distilled. W. P. S.

Estimation of Free Fatty Acids in Fats in the Presence of Soap and Alkaline-earth Soaps. DAVID HOLDE and JULIUS MARCUSSON (*Zeitsch. angew. Chem.*, 1911, **24**, 1945—1948).—In order

to prevent hydrolysis of the soaps, the following process is recommended for the estimation of free fatty acids in mixtures consisting of fat, mineral oil, soap, and calcium or magnesium soaps: Ten grams of the sample are boiled under a reflux apparatus with 50 c.c. of a mixture consisting of 9 vols. of "benzine" and 1 vol. of absolute alcohol until solution of the sample is attained. The hot solution is then filtered, and the filter is washed with a small quantity of the "benzine"-alcohol mixture. The filtrate and washings are now mixed in a separating funnel with 30 c.c. of 50% alcohol (by volume), shaken thoroughly, and titrated with $N/10$-alkali solution, using phenolphthalein as indicator; the end-point of the titration is indicated by the appearance of a pink coloration in the lower layer of the contents of the funnel (compare Abstr., 1910, i, 538). W. P. S.

Analysis of Lactic Acid. W. KLAPPROTH (*Chem. Zeit.*, 1911, 35, 1026—1027).—The following process is recommended for the estimation of lactic acid and lactic anhydride in samples of commercial lactic acid. One gram of the acid is diluted with 20 c.c. of water and titrated with $N/1$-sodium hydroxide solution, phenolphthalein being used as the indicator. The quantity of alkali used corresponds with the lactic acid present, together with one-half of the anhydride. An excess of from 1 to 3 c.c. of the sodium hydroxide solution is now added, the solution is heated for five minutes on a water-bath, the excess of alkali is titrated with $N/1$-sulphuric acid, 1 c.c. of the latter is added in excess, and, after being heated for two minutes on a water-bath, the mixture is titrated with $N/1$-sodium hydroxide solution. The quantity of alkali used in these operations, after allowing for the sulphuric acid added, is equivalent to the second half of the lactic anhydride present. A simple calculation then gives the quantities of lactic acid and anhydride in the sample.

W. P. S.

[**Estimation of Lactic Acid in Blood.**] H. FRIES (*Biochem. Zeitsch.*, 1911, 35, 368—385).—See this vol., ii, 994.

Estimation of Tartaric Acid in Apples, Pears, Cider, and Perry. G. WARCOLLIER (*Ann. Falsif.*, 1911, 4, 485—490).—The author finds that, as a general rule, apples, pears, cider, and perry do not contain tartaric acid. For the estimation of this acid, when present, the method described by Kling (Abstr., 1910, ii, 359) was found to be the most trustworthy. The methods proposed by Berthelot and de Fleuriou, Pasteur and Reboul, Mestrezat (Abstr., 1906, ii, 635), and Muttelet do not yield satisfactory results.

W. P. S.

Detection of Small Quantities of Glycuronic Acid as Osazone. CARL NEUBERG and SUMIO SANEYOSHI (*Biochem. Zeitsch.*, 1911, 36, 56—59).—The phenylosazone of glycuronic acid gives the naphtharesorcinol test (violet-colour when heated with naphtholresorcinol and hydrochloric acid). The colour may be extracted with benzene or chloroform, giving a violet solution. The presence of pentosazones, hexosazones, and disucrosazones does not interfere with the

reaction, since no colour is extracted by the benzene or chloroform in these cases. If ether be used in place of benzene, the extract is always more or less violet with other osazones. In this way, 0·001 gram of glycuronic acid osazone may be detected. W. J. Y.

Estimation of Benzoic Acid. OTTO FOLIN and FRED F. FLANDERS (*J. Amer. Chem. Soc.*, 1911, **33**, 1622—1626).—In an investigation of cranberries, it was found that the benzoic acid could be satisfactorily estimated by titrating a solution in chloroform, from which all the acids except benzoic had been removed, with sodium ethoxide solution.

In attempting to apply this method to the estimation of benzoic acid in ketchup, it was found that several other acids as well as benzoic acid are extracted by the chloroform, and, after numerous experiments, the following method was devised.

The ketchup (25 grams) is placed in a 50 c.c. beaker, 2 c.c. of concentrated nitric acid are added, and about 0·2—0·3 gram of sodium nitrite is introduced in small portions, the mixture being well stirred after each addition. The liquid is rinsed into a 500 c.c. separating funnel by means of 200 c.c. of saturated ammonium sulphate solution, and is then extracted five times with chloroform. The chloroform is transferred to another separating funnel, and shaken with 200 c.c. of a saturated solution of sodium chloride, slightly acidified with hydrochloric acid. It is then transferred to a third separating funnel, again shaken with 200 c.c. of the acidified salt solution, and then run off into a 500 c.c. Erlenmeyer flask and titrated with standard sodium ethoxide solution in presence of a few drops of alcoholic phenolphthalein.

The repeated washing with salt solution does not remove cinnamic acid, and any of this acid which may be present will therefore be estimated with the benzoic acid. The method is rapid and gives satisfactory results. It is also useful as a qualitative test. It is only necessary to shake the chloroform after titration with a small quantity of water, to separate and filter the aqueous solution, and add ferric chloride or apply Mohler's test. E. G.

Apparatus for the Estimation of the Melting Points of Fats. LEO VON LIEBERMANN (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 294—295).—The apparatus consists of a U-tube, the lower portion of which is filled with mercury; the fat under examination is poured in a molten condition into one of the limbs of the tube, and allowed to solidify. This limb is closed by a cork through which pass a thermometer, a platinum wire, and the stem of a small funnel; the bulb of the thermometer and the lower end of the wire are forced into the layer of fat, but do not touch the mercury. The other limb of the tube carries a platinum wire in contact with the mercury. A further quantity of mercury is now poured through the funnel so as to form a layer above the fat, and the tube is heated gradually in a water-bath after the two platinum wires have been connected with an electric bell and battery. When the fat begins to melt, the mercury above it passes downwards and causes the bell to ring by establishing a

t between the two wires. This point is taken as the "in-
g point" of the fat; the point at which the fat becomes perfectly
s the "highest melting point." W. P. S.

Estimation of Fat in Feeding-stuffs by means of Trichloroethylene. R. NEUMANN (*Chem. Zeit.*, 1911, **35**, 1025—1026).—Trichloroethylene is recommended as a solvent in the estimation of fat in such substances as oil-cakes, etc. Five grams of the sample are shaken for thirty minutes with 100 c.c. of the solvent, the mixture is then filtered, 50 c.c. of the filtrate are evaporated, the residue is dried, and weighed. The results obtained agree well with those yielded by the ordinary method of extraction with ether (compare Abstr., 1910, ii, 647). W. P. S.

Detection of Thujone [Tanacetone] in Absinthe. H. ENZ (*Chem. Zentr.*, 1911, ii, 576, 1556; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 337—440; 507—508).—For the detection of tanacetone in any liqueur, a portion of the latter is boiled with the addition of aniline phosphate, in order to destroy aldehydes, and then diluted with water until the alcoholic strength is reduced to 30% by volume. Five hundred c.c. of the solution are fractionally distilled, the distillate being collected in nine portions of 25 c.c. each. In the case of absinthe itself, it is better to reduce the alcoholic strength to 6%, and to collect 50 c.c. quantities of distillate. The portions of distillate, numbers six and seven, are then tested for the presence of tanacetone as described by Duparc (Abstr., 1909, ii, 188); these fractions are free from aldehyde, aniseed oil, and fennel oil. As certain essential oils, such as *Ol. hyssopii, calami, verbenae,* and *sabinae,* and also carvone and citral, give the same reaction as tanacetone, a liqueur which yields a positive reaction does not necessarily contain absinthe; a negative reaction, however, indicates the absence of absinthe.

The second paper is a reply to Philippe and Fellenberg (below).

W. P. S.

Detection of Thujone [Tanacetone] in Absinthe. ERNST PHILIPPE and THEODORE VON FELLENBERG (*Chem. Zentr.*, 1911, ii, 797; from *Schweiz. Woch. Chem. Pharm.*, 1911, **49**, 418—420).—The authors point out several errors in Enz's process (preceding abstract).

W. P. S.

Tannin Solutions. GEORG GRASSER (*Collegium*, 1911, No. 445, 46—52).—The author gives (in tabulated form) the results of treating various concentrations of tannin solutions with the following reagents: (1) Five % solution of tartar emetic; (2) the same with addition of ammonium chloride; (3) with ammonium acetate; (4) a solution containing 5% tartar emetic, 5% sodium chloride, 5% sodium hydrogen tartrate, and 20% sodium acetate; (5) ammoniacal zinc acetate solution; (6) an N/50-iodine solution, and (7) a solution of 10% sodium chloride and 1% gelatin. In very dilute solutions (0·006—0·001%) iodine gives a violet coloration, whereas the others have ceased to give any appreciable reaction, but this varies somewhat with tannins obtained from different barks. F. M. G. M.

General and Physical Chemistry.

Molecular Refraction of Azo-compounds. HENRI DUVAL (*Compt. rend.*, 1911, **153**, 874—875).—The position of substituents in the ring has very little effect on the molecular refraction of aromatic azo-compounds. In the case of azobenzene the index varies somewhat with the solvent, and increases slightly with the temperature; superfusion is without effect. Adopting Brühl's value for nitrogen, the calculated numbers for the molecular refraction with the *D*-sodium and α-hydrogen lines are lower than the actual values found with the lithium line, λ 670·5. W. O. W.

The Negative Pole Spectrum of Oxygen. F. CROZE (*Compt. rend.*, 1911, **153**, 664—665).—A new band, nearer the red than those previously recorded, has been detected in the negative pole spectrum of oxygen. It became visible when the negative electrode had the form of a hollow cylinder, and was resolved into eleven components all diffuse towards the violet. The wave-lengths and relative intensities are given; the most intense component is at λ 6791·3 Ångström units. The five bands now known show a general resemblance to those of nitrogen, but the series cannot be represented by the usual formula. W. O. W.

The Green Carbon Band λ = 5635. RUDOLF KOMP (*Zeitsch. Photochem.*, 1911, **10**, 117—134).—An arc generated by a current of 2—25 amperes at 220 volts was employed as source of light. The intensity of the green carbon band, which appears to be emitted most strongly by that portion of the arc which is in immediate contact with the electrodes, increases with the strength of the current and with the extent to which hissing takes place. In order to avoid cyanogen lines, the arc was surrounded by an atmosphere of carbon dioxide.

The wave-length measurements were made by means of a large concave grating of 6·5 metres radius and 20,000 lines to the inch, and are expressed in 0·001 Ångström units.

The green carbon band is similar in constitution to the second carbon band, which has been previously examined in detail, and this similarity indicates that the two bands have a common origin. Starting from the first head of the band, the spectrum exhibits two series of strong lines and two similar series of finer lines. Between the individual members of these series are a number of relatively weak triplets which seem to fall into six different series. The wave-lengths of the lines of these various series are discussed in reference to the validity of Deslandres' first and second laws. H. M. D.

Separation of Spectra in Compound Gases. G. STEAD (*Phil. Mag.*, 1911, [vi], **22**, 727—733. Compare this vol., ii, 830).—Further experiments are described in which the author has compared the anode and cathode spectra in the discharge through tubes con-

taining ethane, ethylene dichloride, ethylidene dichloride, carbonyl chloride, mercury dimethyl, aniline, ethyl ether, methyl sulphide, and chloroform. The differences between the two spectra indicate that these are determined by the electro-chemical character of the component elements and by the inequality of temperature and of potential gradient at the two electrodes. It is supposed that the discharge of positive ions takes place throughout the negative glow; while negative ions lose their charges in the positive column. H. M. D.

Spectra of the Electrodeless Ring Discharge in Certain Gases. H. DONALDSON (*Phil. Mag.*, 1911, [vi], 22, 720—727).—The influence of pressure, variation in the length of the spark-gap, and frequency of sparking has been investigated for the electrodeless ring discharge in hydrogen, air, carbon dioxide, carbon monoxide, oxygen, and argon. As in the case of the discharge between metal electrodes, it is found that the spectrum is dependent on the intensity of the electric field, although the results are not quite parallel.

In oxygen the continuous spectrum appears at the lowest intensities in the case of the ordinary discharge, whereas the ring discharge intensity lies between those which give rise to the compound line and the band spectra.

In carefully purified carbon monoxide the Swan spectrum appears at high intensities, whereas weak electric fields give rise to the carbon band spectrum only. It is suggested that these two spectra may be the high and low intensity spectra of the same substance.

The ring discharge in nitrogen and air shows no trace of the negative band spectrum, the change from the positive band spectrum to the line spectrum taking place directly. The general results agree with those found for electrode discharge in that the positive band spectrum appears to be brought about by the weakest fields and the line spectrum by stronger fields. H. M. D.

Resolution of the Spectral Lines of Lanthanum and Cobalt in the Magnetic Field. STEPHAN RYBÁR (*Physikal. Zeitsch.*, 1911, 12, 889—900).—From observations of the influence of a strong magnetic field on the lines in the spark spectrum of lanthanum, it is found that the Zeeman effect for certain lines is very similar to that observed in the case of yttrium. The wave-lengths of those lines which exhibit close resemblance in their magneto-optical properties are as follows: La 4575·08, Y 3818·49; La 3921·71, Y 3628·89; La 4946·60, Y 3628·89; La 3381·10, Y 4398·21; La 3193·[illegible], Y 4199·46; La 4986·99, Y 3950·51; La 3303·26, Y 4358·91 and 3195·80. The resolution in the last group of these lines is identical with that observed for the barium line $\lambda = 5997·4$.

The data for cobalt show resolution of the lines 3385·39, 3388·[illegible] and 3463·01 into ten components, of 3495·89, 3550·75, and 3704·[illegible] into eight, of 3491·51, 3561·06, and 3941·05 into seven, of sixteen lines into four, and of 106 lines into three components. H. M. D.

Distribution of Chemical Elements in the Earth's Crust. WLADIMIR J. VERNADSKY (*Bull. Acad. Sci. St. Petersburg*, 1911, [vi], 1007—1018).—[With B. A. LINDENER and E. D. REVUTSKY.]—Table

are given similar to those already published (Abstr., 1910, ii, 1013), and including the results obtained during 1910. In addition to the occurrence of cæsium, rubidium, thallium, indium, boron, etc., in a large number of minerals, that of copper, calcium, strontium, etc., in various artificial products, such as vanadium oxide, yttria, etc., is noted. T. H. P.

The Influence of Neutral Gases on the Absorption of Sodium Vapour. KARL FREDENHAGEN (*Physikal. Zeitsch.*, 1911, **12**, 909—911).—The non-appearance of the principal series lines of the alkali metals when their salts are introduced into the hydrogen chlorine flame has been explained by Franck and Pringsheim (this vol., ii, 574) as due to the small concentration of free electrons. With the object of throwing further light on the nature of the process which gives rise to the principal series lines, the author has investigated the influence of inert gases on the absorptive capacity of sodium vapour. The admission of hydrogen, nitrogen, carbon dioxide, and helium to sodium vapour at 400° increases the absorptive power to a large extent, the magnitude of the influence of the different gases being approximately the same. In each case the intensity and breadth of the *D*-lines increases as the concentration of the admixed inert gas is increased.

Interferometer observations with the yellow helium and mercury lines indicate that the number of absorbing particles in the sodium vapour increases in the presence of the inert gases. This change in the number of the absorbing particles is correlated with the increased ionisation which has been found (compare this vol, ii, 571) to accompany the admixture of sodium vapour with small quantities of inert gases. H. M. D.

Absorption of Light by Silver Hydrosols. NILS PIHLBLAD (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 156—158).—The absorption of light by colloidal silver solutions of different degrees of dispersity has been examined for the mercury lines $\lambda = 404{\cdot}7$, $435{\cdot}9$, $491{\cdot}6$, $546{\cdot}1$, 577—579, 622, and 690. As the size of the particles is gradually increased, the maximum value of the extinction-coefficient moves towards the red end of the spectrum. For all solutions there appears to be, however, a more strongly developed maximum in the ultra-violet region.

From experiments with solutions of variable concentration, it is found that the light absorption takes place in accordance with Beer's law. H. M. D.

Absorption Spectra. IV. Influence of the Solvent and of Dilution on the Validity of Beer's Law. ALFRED W. STEWART and ROBERT WRIGHT (*Ber.*, 1911, **44**, 2819—2826).—The absorbing power of a solution of iodine in alcohol increases at a greater relative rate than corresponds with the increase in dilution of the solution, probably because of the formation of an additive compound between iodine and alcohol. The opposite is the case with solutions of iodine in water; with increasing dilution the solutions become relatively more transparent.

An explanation of the behaviour of aqueous solutions can be given on the assumption that an oxonium derivative is formed which ionises when the solution is diluted; the ionised iodine atom causes practically no absorption, in contradistinction to the alkyl iodides, which show a strong selective absorption (compare Crymble, Stewart, and Wright, Abstr., 1910, ii, 470).

Solutions of iodine in mixtures of water and alcohol can be made more transparent by increasing, and less transparent by decreasing, the proportion of water.

An alcoholic solution of *p*-nitrotoluene behaves similarly to one of iodine, and in this case, also, is the formation of an additive compound possible. The addition of water, however, has simply the ordinary effect of dilution, and does not make the solution relatively more transparent, there being no possibility of an ionisation occurring.

Azobenzene is an indifferent substance, which neither forms additive compounds, nor is capable of ionisation, so that it conforms to Beer's law both in alcoholic and in aqueous-alcoholic solution. T. S. P.

Ultra-violet Absorption Spectra of Nitro-compounds. NICOLAI D. ZELINSKY and N. A. ROSANOFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1173—1183).—The absorption spectra of various nitro-compounds (including nitromethane and nitroethane, for which Baly and Desch [Trans., 1908, **93**, 1747] and Hedley [Abstr., 1908, i, 382] obtained divergent results) and their alkali salts have been investigated in the ultra-violet by Hartley's method (Trans., 1885, **47**, 685).

With nitromethane, in either aqueous or alcoholic solution, the absorption increases considerably in passing from the free nitro-compound to its sodium salt, corresponding with the unsaturated *iso*nitro-derivative.

With nitroethane, the selective absorption is changed into continuous absorption on the formation of the sodium salt. The character of the absorption is the same with nitromethane and nitroethane, but in the latter the absorption band is displaced towards the visible part of the spectrum, probably owing to the influence of the molecular mass; the maxima in the two cases are at $1/\lambda = 3720$ and $1/\lambda = 3640$ respectively. These results confirm those of Baly (*loc. cit.*).

α-Nitropropane gives similar absorption curves, the selective absorption of the free compound being displaced still more towards the visible spectrum, the maximum being at $1/\lambda = 3600$. β-Nitropropane gives a greater general absorption in the free state, and greater selective absorption in the form of sodium salt, than is the case with the α-compound, the maximum lying at $1/\lambda = 3500$; the increased absorption is here evidently due to the yellow colour of the freshly-prepared sodium salt in either aqueous or alcoholic solution.

With tetranitromethane, the selective absorption is still more towards the visible portion of the spectrum, the maximum being at $1/\lambda = 2975$.

ω-Nitrophenylmethane gives a curve similar to those of the above primary nitro-compounds, the maximum being at $1/\lambda = 3465$; the characteristic behaviour of the aromatic series is not shown.

With ω-nitrocyclohexylmethane, selective absorption occurs only with the salts, the maximum being at $1/\lambda = 3440$; the free compound shows marked general absorption.

Free nitrocyclohexane shows two absorption bands with maxima at $1/\lambda = 3500$ and 3720; the salts exhibit general absorption. The same is the case with 1-nitro-1-methylcyclohexane, the maxima being at 3550 and 3740. 1-Nitro-1-methylcyclopentane gives, however, only one absorption band, with a maximum at $1/\lambda = 3570$.

These results confirm the view that the absorption is conditioned, besides by other influences, also by the molecular mass of the compound.

The introduction of nitro-groups into aliphatic compounds causes a considerable increase in the general absorption, along with which selective absorption also appears. The latter is a consequence, not of a quinonoid grouping (compare Hedley, *loc. cit.*), but of the vibration between the elements of the molecule (see Baly and Collie, Trans., 1905, 87, 1332), resulting from the residual valency of the nitro-group. There should hence be no difference in general character between the absorption curves of mono- and dinitro-aliphatic compounds; this is contrary to the results of Hedley, who found no selective absorption for nitromethane, an observation which the author is unable to confirm.

The introduction of nitro-groups into the molecules of hydroaromatic compounds causes marked displacement of the absorption towards the visible part of the spectrum, and also the appearance of absorption bands not observed with the hydrocarbons themselves.

The introduction of nitro-groups into the benzene ring evidently neutralises the residual valency of the nucleus, and weakens the manifestation of molecular vibrations, since the number of absorption bands diminishes. In this respect, the hydroaromatic compounds are similar to the aliphatic compounds, owing to the absence of residual valency.

The conclusion is drawn that the magnitude of continuous and selective absorption is closely connected with the degree of tension prevailing in the molecule. This may depend on the extent of unsaturation of the compound itself, and also on the degrees of tension of its constituent elements. T. H. P.

Photosensitive Antimonite [Stibnite] Cells. WILLIAM SEBASTIAN GRIPENBERG (*J. Amer. Chem. Soc.*, 1911, 33, 1761—1762).—Jaeger (Abstr., 1907, ii, 923) has shown that light has a powerful influence on the electrical conductivity of stibnite. The author has constructed a highly sensitive cell which consists of a lamella of natural stibnite about 0·3 mm. thick, pressed against a glass electrode plate covered with a large number of very fine electrodes of gold or platinum foil, parallel to one another and about 0·067 mm. apart. The width of this grating is 3 × 4 mm., this having about 14 electrodes per sq. mm. The required pressure on the lamella is effected by a small screw-press, into the frame of which insulated wires are fitted. The wires end in small elastic bars, which pinch the electrode-plate and make metallic contact with the bars of the grating.

Such cells have a resistance of from 10^5 to 5×10^6 ohms. The presence of a small oil-lamp in the neighbourhood of the cell causes the resistance to fall to 10% or even 1% of its original value. During the passage of the current, the cells are very sensitive to atmospheric influences, and must therefore be enclosed in vaselin. They can be used satisfactorily for an *E.M.F.* of 30 volts, but if used with very high voltages they are liable to get out of order. E. G.

Absorption and Secondary Radiation of Cathodic Rays. F. BUTAVAND (*Ann. Chim. Phys.*, 1911, [viii], **24**, 421—432. Compare Schmidt, Abstr., 1910, ii, 7, 378; Schmidt and Cermack, Abstr., 1910, ii, 918).—When a group of β-rays falls on a plate of an elementary substance $I = I_0 e^{-\lambda d}$, where I is the intensity of a saturating current, I_0 that of the emergent group of rays, and λ the coefficient of absorption. λ is not proportional to the density, ρ, of the element. The expression $\lambda/\rho = kP^{1/3}$, where P is the atomic weight, gives values of k which fluctuate about a mean 1·85 when values of λ, ρ, and P are inserted for the various elements. Taking any one of the groups of the periodic table, the differences between 1·85 and the values of k found for the constituent elements are alternately positive and negative, so that k is a periodic function of the valency V. Substitution of values in the expression $\lambda/\rho = 1{\cdot}88P^{1/3}(1 \pm 1/10 \cos \omega V/8)$ gives values approximating to those calculated. For compounds, an analogous expression holds, namely, $\lambda/\rho = hp^{1/3}$, where p is the molecular weight and h a coefficient which is approximately constant for analogous compounds. For applications of this the original should be consulted.

β-Rays falling on a plate of an elementary substance give rise to secondary β-rays in all directions, and the intensity η of these secondary rays varies with the nature and substance of the plate, and increases with the atomic weight P of the element. Substitution of values in the expression $\eta = k'P^{1/3}$ shows that k' is approximately equal to $10k$. T. A. H.

Radioactive Properties of High Temperature Flames. HARRY CARTER (*Phil. Mag.*, 1911, [vi], **22**, 805—816).—To ascertain whether atomic disintegration takes place in reactions which are accompanied by the liberation of large quantities of energy, the author has examined the electric arc, the spark, and the oxy-hydrogen and oxy-acetylene blowpipe flames for β-radiation. The apparatus was arranged so as to avoid temperature variations of the electroscope and the presence of ionised air in its neighbourhood. In no case could any appreciable difference be detected between the rate of leak when the electroscope was exposed to the source and when shielded from its action.

H. M. D.

Radiation in Explosions of Coal Gas and Air. W. T. DAVID (*Phil. Trans.*, 1911, *A*, **211**, 375—410).—Measurements have been made of the radiation emitted during the explosion and subsequent cooling of mixtures of coal-gas and air. By the use of screens of fluorite, quartz, glass, and water for the bolometric apparatus, it was possible to estimate fairly accurately the total radiation emitted by the gas, the approximate proportions emitted by water vapour and by

carbon dioxide, and also the amount of energy in the luminous radiation.

The bolometric records show that, for different gas mixtures at atmospheric pressure, the total heat lost by radiation to the walls of the vessel up to the moment of maximum pressure is approximately proportional to the product of the third power of the maximum absolute temperature by the time of explosion. The total radiation lost during the explosion and subsequent cooling is about 25% of the heat of combustion of the gas present in the explosion chamber. The radiation in the initial stages of cooling is a function of the time interval from ignition as well as of the temperature. The rate at which the radiation is emitted is a maximum some time before the attainment of maximum pressure, and probably occurs at the moment when the flame fills the explosion chamber. Weak explosive mixtures radiate very much more in the initial stages of cooling than stronger mixtures do when these have cooled to the same temperatures.

The total heat radiated by carbon dioxide is about twice as large as that radiated by an equal volume of water vapour at the same temperature.

When explosive mixtures of the same strength, but of different densities, are compared, it is found that the ratio of the heat which is lost by radiation up to the moment of maximum pressure to the heat of combustion decreases as the density increases, but denser mixtures emit much more strongly at the moment of maximum pressure and in the initial stages of cooling.

In the second part of the paper an account is given of experiments relating to the diathermancy and emissive power of the hot gaseous mixtures after explosion. H. M. D.

The Distribution of the Intervals of Emission of the α-Particles of Polonium. (Mme.) MARIE CURIE (*Le Radium*, 1911, 8, 354—356).—The results obtained confirm those of previous observers (Rutherford and Gieger, Abstr., 1910, ii, 917; Marsden and Barratt, *Proc. Phys. Soc.*, 1911, 23, 367). From a series of curves, obtained by means of the ionisation method in which the excursions of the electrometer needle are recorded on a moving photographic film, comprising 1080 intervals, it was found that the number of intervals, n, comprised between t and $t+\theta$, where θ represents a fixed time, varies according to an exponential law, $n = n_0 e^{-t/\tau}$, where τ is the mean interval, and $n_0/\theta = N/\tau$, N being the total number of intervals. This is the same law as applies to the free path of the molecules of a gas, the mean free path corresponding with the mean interval between the emissions. F. S.

The Variation of the Activity of Some Radioactive Substances with Time. (Mme.) MARIE CURIE (*Le Radium*, 1911, 8, 353—354.)—The α-rays of uranium oxide have been kept under observation for four years. The means of the measurements taken in each year agree within 0·5%, and the conclusion may be drawn that the activity has remained constant. The β- and γ-rays from a salt of barium containing radium, previously purified from radio-lead and its products, and contained in a thin-walled glass tube covered with aluminium foil, have been observed for twenty months. The tube forms the central electrode in a cylindrical ionisation chamber, and a

correction is introduced for the changes of density of the air. An increase of the radiation amounting to about 2·5% per year has been observed, which is doubtless due to the formation of radio-lead. A preparation of Debierne's actinium many years old has been studied in the same way. The measurements are unaccountably irregular, but indicate a diminution of the penetrating rays in three years amounting to 10% of the initial activity. Either there must exist between actinium and radioactinium an intermediate substance of long-life giving β-rays, initially present in excess, or the period of average life of actinium is only of the order of thirty years. In the latter case the relation between actinium and the other radio-elements of uranium minerals ought to be capable of elucidation. Radio-lead submitted to a crystallisation of the chloride to remove radium-E and -F, and containing initially radium-D only, has been studied for five years. The penetrating rays attained the maximum in one month, the period of radium-E being 4·7 days, and the α-rays attained the maximum in two years. Both types of radiation remained fairly constant during the third year. During the fifth year a regular decay of the α-rays occurred, amounting to about 5% in 440 days. This would correspond with a period of average life of radium-D of about twenty-five years. The β-ray measurements are less precise, but indicate about the same rate of decay. All measurements have been effected by means of the quartz piézo-électrique, which remains, when properly mounted, absolutely constant, and is very suitable for these measurements.

F. S.

Thorium and its Products of Disintegration. May Sybil Leslie (*Le Radium*, 1911, 8, 356—363).—The results confirm those of other workers as to the chemical nature of mesothorium. The material employed was thorite containing 40% of thorium oxide and 0·73% of uranium. In the electroscope employed the different values for the separate α-ray producing members of the series were: thorium 5·5%, radiothorium 9·4%, thorium-X 12·2%, emanation 48%, thorium-A 12·2%, thorium-B 12·2% (old nomenclature). This accords with the view that the emanation gives four α-particles per atom disintegrating, and that the α-rays due to thorium itself have a very low velocity corresponding with a range of only about 2 cm. The activity of oxide of thorium freshly separated from thorium decays at a rate which indicates that the period of radiothorium is only three or four months.

F. S.

The Amount of Radium Emanation in the Soil and its Escape into the Atmosphere. John Joly and Louis B. Smyth (*Sci. Proc. Roy. Dubl. Soc.*, 1911, 13, 148—161).—Observations have been made in the vicinity of Dublin, during the months of April and May, 1910, of the amount of radium emanation in the soil at various depths and on the amount exhaled per hour from the surface. The period covered began with wet and stormy weather and ended with a long spell of fine settled weather. The observations are in agreement with the view that the influence of rain is to choke the capillaries of the soil, retarding the escape of the emanation and therefore increasing the amount in the soil, whilst reducing that in the air. At depths

below the surface of from 25 to 250 cm., the relative amount of emanation in the air in the soil was usually many thousand times that in the atmosphere. A very rapid escape of emanation from the soil was established, and it is considered probable that this exhalation is the chief, if not the only considerable, source of the emanation in the atmosphere. F. S.

Quantity of Radium Emanation Liberated From One of the Springs at Columbières-sur-Orb (Hérault). JACQUES DANNE and VICTOR CRÉMIEU (*Compt. rend.*, 1911, **153**, 870—871).—This spring evolves gas at the rate of 43,000 litres per day, with an amount of radium emanation corresponding with 860 mg.-minutes per twenty-four hours. This unusually large amount of emanation is readily available in an active form, since the gas contains 95% of easily removable carbon dioxide. W. O. W.

The Radioactivity of Mineral Springs. ERICH EBLER and M. FELLNER (*Zeitsch. anorg. Chem.*, 1911, **72**, 233—301).—The gas obtained from the Max mineral spring of Dürkheim contains 6.1×10^{-9} cubic mm. of radium emanation per litre. The spring evolves 30 litres of gas per hour. The activity of the sediment is, as usual, variable, and about one-half of the activity disappears when the sediment is gently warmed. An estimation of the radium present by Strutt's method gives, for two samples of sediment collected at different times, 3.03×10^{-10} and 1.76×10^{-10} gram radium per gram of sediment. Other radioactive substances, including radiothorium, are also present.

An analysis of the sediment, dried at 106°, shows that it contains 45.5% SiO_2, 9.9% residue insoluble in hydrofluoric acid, 10.7% As_2O_3, 7.1% CaO, 15.7% Fe_2O_3, and 2.5% Mn_3O_4, with small quantities of other substances. Sulphates are absent, and carbonates present only in minute quantity. Lead is present to the extent of 0.1%. Thorium and uranium are absent. The proportion of potassium increases with the time of agitation with the water, whilst that of sodium is unchanged. When treated with hydrochloric acid, 91% of the radium remains in the insoluble residue, being adsorbed by colloidal silica. Boiling hydrochloric acid extracts a substance from the sediment, which crystallises in polyhedral, yellow leaflets, 600 grams being obtained from 10 kilograms of sediment. This quantity yielded 33 grams of potassium nitrate, of similar activity to ordinary potassium salts.

The water itself contains 0.97×10^{-10} gram of radium per litre. The mother liquor obtained in the commercial crystallisation of salts from this water is distinctly radioactive, the activity being due to radium. Determinations of the activity of the sediment and of the mother liquor give a value of 0.78×10^{-10} gram of radium per litre of the original water, in good agreement with the foregoing.

Details are given of the chemical methods of investigating these and similar products. C. H. D.

The Radioactivity of the Mineral Springs of Tyrol. III. MAX BAMBERGER and KARL KRÜSE (*Monatsh.*, 1911, **32**, 797—813. Compare Abstr., 1910, ii, 570).—A table is given of numerous

determinations of the activity in Mache units of mineral springs in Tyrol. The table contains details also of the temperature of the spring and of the rock in which it occurs. F. S.

The Radioactivity of the Air Over the Open Sea. CARL RUNGE (*Chem. Zentr.*, 1911, ii, 786; from *Nachr. K. Ges. Wiss. Göttingen, Math.-physikal. Klasse*, 1911, 99—109).—Under similar conditions the induced activity of the atmosphere was found to be about as great in the middle of the Atlantic Ocean as near the coast. In both cases the decay curve for the first two hours is that of radium alone, except that in the middle of the ocean the decay for the first half-hour is somewhat more rapid. After two hours the decay becomes slower, indicating the presence of thorium. F. S.

The Formation of Positive Ions by Heated Metals. Z. KLEMENSIEWICZ (*Bull. Acad. Sci. Cracow*, 1911, *A*, 417—424).—The emission of positive ions by electrically heated platinum, palladium, gold, iridium, copper, iron, and tungsten wires has been investigated. From measurements of the leakage current between the wire and a surrounding metal cylinder after different time intervals, decay curves were obtained for new wires, and also for wires which had been heated in a vacuum or left in contact with strongly compressed gases for several hours. In the case of platinum, observations were also made with the metal after anodic and cathodic polarisation.

The experimental data are in favour of the view that the positive ion emission is mainly due to absorbed gases. It is calculated that about 1% of the gas molecules which leave the heated metal are electrically charged. This fraction is approximately constant, and, as a consequence, the number of positive ions will be proportional to the solubility of the gas in the metal under investigation.

Experiments with palladium and iridium, superficially covered with the corresponding oxides, indicate that emission of ions is not an accompaniment of the formation or dissociation of these oxides. On the other hand, tungsten, copper, and iron show emission effects, both during oxidation and reduction. H. M. D.

Mobility of Positive Ions Produced from Heated Aluminium Phosphate in Gases at Low Pressures. GEORGE W. TODD (*Phil. Mag.*, 1911, [vi], 22, 791—804).—The mobility of the positive thermions from aluminium phosphate has been measured in air, carbon dioxide, sulphur dioxide, methane, and hydrogen at low pressures. As the pressure is lowered, the mobility increases in such a way that the product of pressure and ionic mobility remains approximately constant, but increases much more rapidly than this when the pressure is lowered beyond a certain critical value. This rapid increase may be due to the disintegration of the molecular clusters which form the ions under higher pressures, or to the existence of a positive ion in the free condition for short intervals of time. In air and carbon dioxide the data obtained at the lowest pressures show that the positive charge is carried by particles, the mass of which is smaller than that of the ordinary gas molecules.

Water vapour has only a small influence on the mobility of the positive ion in the region where the inverse pressure law holds, but has a large effect at smaller pressures. Under these conditions, the presence of water vapour causes the mobility to fall below the value which would correspond with the inverse pressure law.

The thermions emitted by heated aluminium phosphate appear to yield by collision with the gas molecules the same ions as are produced by the action of *X*-rays on the gas. H. M. D.

Positive Ionisation from Hot Salts. OWEN W. RICHARDSON (*Phil. Mag.*, 1911, [vi], 22, 669—703. Compare Abstr., 1910, ii, 923; this vol., ii, 9, 10)—The nature of the positive ions emitted by heated salts has been further examined by experiments with two different forms of apparatus and observations at different pressures and temperatures. The values obtained for e/m indicate that the positive ions are metallic atoms which are not necessarily atoms of the metal in the salt under examination, but may be due to some other metal present as impurity. In the case of aluminium phosphate strong evidence has been obtained in favour of the view that the observed $e/m = 32$ is due to traces of foreign substance, for when the aluminium phosphate was prepared from ammonia, aluminium chloride, and phosphoric oxide, all of which had been subjected to distillation before use, a product was obtained which only gave about 1/150 of the emission given by Kahlbaum's aluminium phosphate.

In regard to the relative efficiency of different salts in emitting positive ions, it appears that the emissive power increases with the electro-positive character of the metallic constituent and with the volatility of the compounds which appear to be formed from the original substance at the high temperature. A number of facts cannot be satisfactorily explained unless it is assumed that the ionisation is not directly due to the heated salt, but to the action of vapours emitted by the salts on the hot platinum. This is the case for the changes in the emissive power which are observed when the pressure of the gas is altered and for the different effects which are obtained according to whether the salt is supported on a strip of platinum or is contained in a platinum tube. H. M. D.

Specific Conductivity of Fused Potassium Nitrate. A. H. W. ATEN (*Zeitsch. physikal. Chem.*, 1911, 78, 1—23).—The apparatus used was similar to that of Lorenz and Kalmus (compare Abstr., 1907, ii, 430). The thermostat contained fused potassium and sodium nitrates, and the temperatures were measured by means of a carefully calibrated platinum resistance thermometer. The determination of the resistance capacity of the apparatus and the corrections made are described in detail.

Measurements were made at intervals of temperature between 340° and 500° in vessels of common glass, Jena glass, and quartz respectively. The results for the different vessels are in fair, but not in exact, agreement; no satisfactory explanation for the deviations has been found. At high temperatures the conducting values are higher than those found by Lorenz and Kalmus, but are in fair agreement with those of

Goodwin and Mailey (*Phys. Review*, 1908, 26, 28); at low temperatures, on the other hand, the author's results are lower than those of Goodwin and Mailey. The following numbers show the variation of the specific conductivity with temperature: 0·6334 at 340°, 0·8301 at 400°, 0·9687 at 450°, and 1·1099 at 500°. G. S.

Electrical Conductivity of Liquid Sulphur Dioxide Solutions at −33·5°, −20°, −10°, 0°, and +10°. Edward C. Franklin (*J. Physical Chem.*, 1911, 15, 675—697. Compare Abstr., 1909, ii, 337). —The conductivity of solutions of potassium iodide and bromide, tetramethylammonium iodide, ammonium thiocyanate, ethyl ammonium bromide, and dimethylammonium chloride in liquid sulphur dioxide has been measured, using the apparatus and methods previously described for liquid ammonia.

The conductivity-dilution curves closely resemble those given by liquid methylamine and liquid ammonia. On diluting the saturated solutions, the molecular conductivity rises to a maximum, then declines to a minimum at moderate dilutions, and finally rises continuously to the highest dilutions measured, approaching a maximum value in the normal way.

It is suggested that the high conductivity in concentrated solutions is due to autoionisation of the salt, whereas in dilute solutions ionisation by the solvent comes into play. The initial increase in conductivity on diluting saturated solutions is attributed to the considerable fall in viscosity which more than compensates for the fall in autoionisation. The temperature-coefficient of conductivity is positive for very concentrated and very dilute solutions, whilst for solutions of intermediate concentration the temperature-coefficient is generally reversed. The autoionisation in concentrated solutions and the almost complete ionisation at high dilutions are presumably unaltered by temperature changes which influence the conductivity only through the viscosity. At moderate dilutions the ionisation by the solvent may suffer a marked diminution, with rise in temperature.

It was observed in the course of the experiments that potassium bromide is more soluble in liquid sulphur dioxide the lower the temperature. R. J. C.

Electrical Conductivity of the System Ferric Chloride-Ammonium Thiocyanate. Corrado Bongiovanni (*Boll. Chim. Farm.*, 1911, 50, 694—697).—The conductivity of a red solution containing ferric chloride and ammonium thiocyanate is approximately equal to the sum of the conductivities of solutions of the separate salts of corresponding concentrations. The slight diminution in the degree of dissociation which occurs is probably due to mass action between the reacting salts, and consequent formation of a small number of undissociated molecules. Indeed, if the salts are taken in equivalent proportions, and in solutions sufficiently dilute to ensure complete dissociation, the specific conductivity of the red solution becomes very nearly equal to the sum of the separate conductivities.

These results confirm Magnanini's interpretation (Abstr., 1891, 1150) of this reaction (compare also Abstr., 1907, i, 833; 1908, i,

1907, and are not in agreement with the view advanced by Tarugi (Abstr., 1905, i, 176). T. H. P.

The Electric Vacuum Furnace. OTTO GOECKE (*Metallurgie*, 1911, 8, 667—676).—The carbon tube electric vacuum furnace (Ruff and Goecke, this vol., ii, 897) has been further improved by the addition of a second carbon tube, enclosing the first and insulated from it by means of magnesia, to lessen the loss of heat by radiation. The crucible may be introduced and removed without removing the heating tube. A series of determinations of melting points in this furnace by means of the Wanner optical pyrometer gives results in good agreement with previous observations. A few new determinations have been made. Alumina has m. p. 2020—2035°, either in a vacuum or in nitrogen. Lime has not been fused in a vacuum, but in nitrogen it melts at 1990°, owing to a chemical reaction. Magnesia boils, without melting, at 2029°/7 mm., but volatilisation begins in nitrogen at atmospheric pressure at 1805°. C. H. D.

Differences in Potential of Apparent Contacts between a Metal and Electrolytic Solutions. J. GUYOT (*Compt. rend.*, 1911, 153, 867—869. Compare Abstr., 1908, ii, 656).—The apparent difference in potential established by ionising air between the surfaces of a salt solution and a metal plate above it varies with the logarithm of the ionic concentration of the solution. For solutions of the alkali chlorides, using reversible electrodes, the difference of potential is given by the expression $V = V_0 \pm 0.053 \log c.1/p$. This is analogous to the Helmholtz formula for the electromotive force of a couple consisting of two reversible electrodes immersed in a liquid. W. O. W.

Polarisation of Solid Electrolytes. [The Phenomena of Passivity.] FRITZ HABER and J. ZAWADZKI (*Zeitsch. physikal. Chem.*, 1911, 78, 228—243).—When solid compressed silver salts (the chloride, bromide, iodide, and sulphate were used) are electrolysed between plates of silver, considerable polarisation occurs, and this is the greater the lower the temperature. With silver sulphate at room temperature, for instance, an *E.M.F.* of polarisation of 0·312 volt was observed two minutes, and 0·125 volt twenty minutes after breaking the current. At −80° a polarisation *E.M.F.* of 1·562 volts was observed one minute after breaking the current. Salts which have been kept compressed for some time give higher values than pastilles freshly prepared. By means of experiments with other electrodes it is made probable that the polarisation occurs only at the anode.

These results cannot be reconciled with the usual assumption that the primary change at the anode is the formation of silver ions from metallic silver. It is suggested that the transport of the current from solid electrolyte to anode is effected by the passage of electrons with simultaneous formation of oxidising substances (silver persulphate from silver sulphate, free halogen from halogen ions). These oxidising substances then attack the silver anode, this secondary

reaction being greatly retarded by cooling. It is probable that the mechanism is the same in aqueous solution, but in this case the discharged ion in presence of the solvent reacts rapidly with the electrode. These results may have an important bearing on the phenomena of passivity. G. S.

Galvanic Elements with Carbon Anodes. P. Beutner (*Zeitsch. Elektrochem.*, 1911, 17, 851—877).—This is a very detailed investigation of the Jacques cell and of several modifications of it. The separate potentials of carbon on the one hand, and of a number of metals on the other, in fused sodium hydroxide are determined over a considerable range of temperature. The potential of carbon in fused sodium hydroxide referred to the calomel electrode is about 1 volt at 370°, and increases by 0·00184 volt per degree. The addition of small quantities of sodium nitrate or perchlorate diminishes the potentials. Permanganate has no effect, since manganate is always present. The potentials in fused mixtures of alkali carbonates are smaller by about 0·8 volt.

The metals iron, nickel, cobalt, silver, copper, constantan, gold, and platinum all become passive in fused sodium hydroxide, and give very exactly the same potentials. These are 0·5 volt at 550°, with a temperature-coefficient of 0·00096 volt per degree between 350° and 650°.

The observed *E.M.F.*'s of the Jacques cells (carbon | fused sodium hydroxide | passive metal) were at 350°, 0·633 volt; at 450°, 0·722 volt; at 550°, 0·804 volt; at 650°, 0·875 volt. These numbers agree well with those calculated from the separate potentials.

The polarisation of the electrodes is then studied. When the cell is yielding a current, the carbon is the anode and the passive metal the cathode, hence the anodic polarisation of the carbon and the cathodic polarisation of the metal are alone of practical interest.

Carbon is readily polarised anodically, a current of 0·06 ampere per sq. cm. reducing its potential by about 0·5 volt at 395°. The addition of sodium nitrate, perchlorate or chlorate diminishes the polarisation considerably, and the latter does not reduce the potential, but they all decompose about 400°, and are consumed. The depolarisation produced by the addition of selenium or tellurium to the electrolyte is of a different kind. The addition of 5% of selenium reduces the polarisation to very small values, and the effect is permanent. Neither selenites nor selenates have this effect; it is therefore ascribed to the presence of a selenide. Tellurium appears to be even more active.

In fused sodium hydroxide, silver and platinum give almost the same cathodic polarisation curves, whilst iron and nickel are much more strongly affected, probably because they become active. The most effective depolariser is sodium peroxide.

When carbon rods are used as anodes in fused sodium hydroxide to which 3% of selenium has been added, their loss of weight varies between 77 and 90% of that calculated, on the supposition that the electrochemical equivalent of carbon is 3.

As Haber had already observed, the Jacques cell gives a small and

inconstant *E.M.F.* if the electrolyte is free from manganate. This is confirmed using fused lithium hydroxide as electrolyte in presence of a manganate; the *E.M.F.* is the same as with sodium hydroxide. A number of cells with aqueous solutions of sodium hydroxide containing a little potassium permanganate were also measured at temperatures down to 95°. Their *E.M.F.*'s lie on the continuation of the curve obtained with the fused electrolyte at higher temperatures. Above about 650° the *E.M.F.* of the cells falls off rapidly.

A number of cells of different types were tried at high temperatures; most of these gave small and inconstant *E.M.F.*'s. Elements of the type carbon | fused boron trioxide | platinum, in which oxides of iron, nickel, cobalt, silver, or copper were added to the electrolyte gave *E.M.F.*'s between 1000° and 1300° of as much as 1 volt.

T. E.

Electrical Properties of Alkali Metals, Rhodium, and Iridium. WITOLD BRONIEWSKI and L. HACKSPILL (*Compt. rend.*, 1911, 153, 814—816. Compare Abstr., 1910, ii, 821; Bernini, Abstr., 1908, ii, 255).—The alkali metals were of greater purity than those employed by other observers, and were distilled in a vacuum. The following expressions give the thermoelectric powers when copper is the second metal, for the temperature interval 0° to −183°. Cs $+0·66 - 0·0010t$, Rb $-8·26 - 0·0302t$, K $-11·33 - 0·0376t$, Na $-4·16 - 0·0144t$. In the case of cæsium and rubidium, the variation of thermoelectric power with temperature was also registered photographically, using a Le Chatelier galvanometer. The curve for cæsium shows a break in the neighbourhood of the melting point of the metal, whilst that for rubidium shows an angular point.

Similar measurements were made with rhodium and iridium, using lead as the second metal. For the temperature interval −78 to −100°, the values for the thermoelectric powers are given by the expressions: Rh $+ 2·17 + 0·0005t$, Ir $+ 2·44 - 0·0014t$. At 80°, rhodium appears to undergo a molecular transformation analogous to that of copper, the electrical resistance being much below the expected value.

W. O. W.

Thermoelectric Forces in the Transition from the Solid to the Liquid State of Aggregation. PAUL CERMAK and HANS SCHMIDT (*Ann. Physik*, 1911, [iv], 36, 575—588. Compare Koenigsberger and Weiss, this vol., ii, 578).—The variation of the thermoelectric potential of the elements tin–constantan, tin–iron, and lead–constantan with temperature has been examined at temperatures above and below the melting points of tin and lead. In each experiment two junctions were employed, one of these being kept at a constant temperature below the melting point, whilst the other was slowly heated or allowed to cool, so as to cause the tin or lead to change its state of aggregation. Potential and temperature measurements were made at suitable intervals, and curves have been constructed to show the connexion between thermoelectric potential and the difference between the temperatures of the two junctions. From the results thus obtained, it appears that the change from solid

to liquid is not accompanied by any break in the thermoelectric potential, or by any alteration in the temperature-coefficient of the thermoelectric effect. H. M. D.

Anodic Behaviour of Nickel in Presence of Chromous Salts. C. Russo (*Gazzetta*, 1911, **41**, ii, 101—109. Compare this vol., ii, 181).—The theory that the anodic polarisation of nickel is due to the formation of a solid solution of oxygen at its surface does not exclude the possibility of polarisation even in a solution containing a strong reducing agent, because an oxidising layer can form in the vicinity of the electrode, and there is nothing but the diffusion of the reducing substance to prevent the oxidation of the electrode in consequence. Accordingly, the author finds that the presence of a chromous salt makes it more difficult for nickel to attain to the passive state, but does not prevent its doing so. To bring the condition about in a short time, a much stronger current is required than in the absence of a chromous salt, but if the current is then diminished, no loss of passivity is observed. The presence of the reducing agent also modifies but slightly the polarisation values. Further experiments have shown that the free acetic acid present in the solution containing the chromous salt used in the above electrolysis does not affect the polarisation in any way. This is due to its not taking part in the electrolysis, for in a solution of sodium acetate and acetic acid the polarisation does not follow the logarithmic law, whilst if this same solution contains sodium sulphate the logarithmic law is again valid. R. V. S.

The Flame Arising from the Nitrogen-burning Arc. Robert J. Strutt (*Proc. Roy. Soc.*, 1911, *A*, **85**, 533—536).—The structure of the high-tension alternating arc in hydrogen, nitrogen, oxygen, and air has been examined. In the case of the pure gases, the luminosity is entirely due to the true current-carrying arc, but in air the arc is accompanied by an envelope of yellowish-green flame, which may rise to a considerable height above the arc, and terminates above in quite a sharp point like a candle flame. The luminosity of the arc proper is very small in comparison with that of the flame, but, since the flame gives no violet rays, the arc may be seen alone by examination through a deep violet glass. It then appears to be of about the same size and form as the arc in pure nitrogen. By reduction of the air pressure the distinction between the arc and the flame can be made more evident. Under these conditions, a rose-coloured arc is seen, which is separated from the surmounting yellowish-green flame by a slight dark interval. The phenomenon is further accentuated if the reduction in pressure is accompanied by an increase in the percentage of oxygen.

The behaviour of the arc flame indicates that the luminosity effect is identical with the after-glow sometimes observed in Geissler tubes filled with air. This has been shown to be due to the oxidation of nitric oxide by ozone (*Proc. Phys. Soc.*, 1910, **23**). It has been observed since, that nitrogen peroxide gives the same result with ozone, and the author draws the conclusion that the yellowish-green

...ase of the arc is due to the interaction of ozone and oxides of nitrogen which are formed in the arc itself. H. M. D.

Formation of Hydrogen Cyanide in the High Tension Electric Flame. I. MOSCICKI (*Zeitsch. Elektrochem.*, 1911, 17, 877).—Polemical. Lipinski obtained the information published (this vol., i, 849) while working in the author's employment in a confidential capacity. T. E.

The Magnetic Properties of Some Nickel Steels. EDWARD ...OWER GLAUERT and SIEGFRIED HILPERT (*J. Iron Steel Inst.*, 1911, 83, 375—411).—Alloys of iron with 5·86, 24·32, and 32·90% of nickel have been examined after slow cooling from 1250°, and also after quenching from 600°, 900°, and 1240°, and after cooling to −50°, −100°, and −180°, a magnetometric method being used. The 6% steel is unchanged by quenching from 600° or by cooling, whilst quenching from 900° renders it martensitic, and greatly increases the coercive force. If quenched from 1240°, it is only partly martensitic, and is magnetically softer. The 25% steel is apparently non-magnetic in the stable condition, but becomes magnetic at low temperatures, no sharp critical point being observed. This alloy, quenched from 1240°, becomes as magnetic at −180° as that cooled slowly. It is suggested that a highly magnetic substance is formed at high temperatures, which dissociates between 600° and 900°, but may re-form on slow cooling. The structure of specimens quenched from 600° resembles that of natural meteoric irons, and when cooled to low temperatures becomes similar to that of quenched high-carbon steels. The 33% steel is little altered by quenching, and is not changed by cooling below zero. The structure is polyhedral, but etching with sulphurous acid develops a duplex structure, like that of the last alloy. It is improbable that γ-iron is non-magnetic. C. H. D.

Influence of the Magnetic Field on Passive Nickel and Iron. HORACE G. BYERS and AGNES FAY MORGAN (*J. Amer. Chem. Soc.*, 1911, 33, 1757—1761).—It has been shown by Byers and Darrin (Abstr., 1910, ii, 579) that when iron is used as an anode in various electrolytes, the current density required to produce the passive state is increased when the anode is placed in a magnetic field. It has now been found that the same is true in the case of nickel.

Magnetised steel is more difficult to render passive than the same steel which has not been magnetised, and soft steel is affected to a greater extent than hard steel. This is in accordance with the observations of Andrews (Abstr., 1893, ii, 16).

The positive pole of the magnets is rendered passive more easily than the negative pole. E. G.

Magnetisability of the Salts of Metals of the Iron Group. RUDOLF H. WEBER (*Ann. Physik*, 1911, [iv], 36, 624—646).—In continuation of previous experiments (Abstr., 1906, ii, 331), the author has measured the magnetic susceptibility of chromous and chromic chlorides and of cobaltous and cobaltic sulphates. The atomic

susceptibilities of the metals in these compounds are respectively: Cr in $CrCl_2$, 0·01078, in $CrCl_3$, 0·00625; Co in $CoSO_4$, 0·01015, in $Co_2(SO_4)_3$, 0·00486. As in the case of manganese, the susceptibility of bivalent chromium and cobalt is greater than that of the tervalent metal, whereas the reverse is true for iron. H. M. D.

Use of the Magnetic Field in Determining Constitution. XI. PAUL PASCAL (*Bull. Soc. chim.*, 1911, [iv], 9, 868—872. Compare this vol., ii, 850).—An extension of the study of anomalous cases (*loc. cit.*) to colouring matters. The magnetic susceptibilities of the aminoazo-compounds even after fusion and rapid cooling indicate that they possess the azo- and not the quinonoid structure. Similarly, the magnetic susceptibility of magenta is in accordance with Rosenstiehl's formula.

The hydroxyazo-compounds exist in two forms having different densities: the one is yellow to orange-coloured and stable in the cold, the other reddish and stable on heating. Both co-exist in some cases. Consequently, the magnetic susceptibilities observed for the hydroxyazo-compounds vary with the treatment to which the substances have been subjected. In the fused state, or after fusion and rapid cooling, the magnetic susceptibilities are high, and are in accordance with a quinonoid constitution. After deposition from solution or after fusion and slow cooling, the magnetic susceptibilities are low, and indicate that the paler coloured forms have the azo-constitution.

The magnetic susceptibility of aurin indicates that it is quinonoid in structure.

The formulæ assigned by Torrey and Hunter (Abstr., 1907, i, 1030) to the two forms of the silver derivative of tribromophenol are in harmony with their magnetic values. T. A. H.

Magnetic Study of the Rôle of Water in the Constitution of Solid Hydrates. (Mlle.) E. FEYTIS (*Compt. rend*, 1911, 153, 668—671. Compare this vol., ii, 367).—The coefficient of magnetisation of salts in the anhydrous and in the hydrated condition has been measured to ascertain whether water of crystallisation has any effect on magnetic susceptibility. For the sulphates of cobalt, samarium, and gadolinium, the property is strictly additive, the observed values for the anhydrous substances agreeing with the numbers found by deducting the coefficient for water from that of the crystalline hydrated salt. In the case of copper sulphate, however, although the $4H_2O$ lost at 100° is without influence on the magnetic properties of the anhydrous compound, the remaining molecule, regarded as water of constitution, does not obey the law of additivity, since the coefficient for the anhydrous salt is identical with that of the monohydrate.

W. O. W.

Expansion Pressure of a Normal Liquid. L. GAY (*Compt. rend.*, 1911, 153, 722—724. Compare Abstr., 1910, ii, 935, 1043; this vol., ii, 850).—The author develops the expression:

$$\log \pi = \log (RT/V - b) + b(V - b) - (EL - RT + PV)/RT,$$

wherein π is the expansion pressure of a liquid at constant temperature, T, of molecular volume, V and co-volume, b, L being the ideal molecular latent heat. Application to benzene shows that this furnishes a simple method for characterising normal liquids, or for determining the co-volume and internal pressure. Biron's determinations of the vapour density of benzene (Abstr., 1910, ii, 393) and Young's values for vapour pressure (Trans, 1889, **55**, 486) were employed. The results were in close agreement with theory.

W. O. W.

Specific Heat and the Theory of Finite Increments of Energy. WALTHER NERNST and F. A. LINDEMANN (*Zeitsch. Elektrochem.*, 1911, **17**, 817—827. Compare this vol., ii, 465, 466). —The difference between the atomic heats calculated by Einstein's ormula and those observed at low temperatures is discussed. The uggestion that all the atoms of a substance do not have the same requency of vibration is dismissed, because all the atomic heat curves ay be superposed by using a suitable temperature scale, and because Rubens and Hollnagel's measurements of the infra-red absorption ands of sodium and potassium chloride and potassium bromide show here to be quite narrow (Abstr., 1910, ii, 172). The author's new ormula: $C_v = 3R/2\{(\beta v/T)^2 e^{\beta v/T}/(e^{\beta v/T}-1)^2 + (\beta v/2T)^2 e^{\beta v/2T}/(e^{\beta v/2T}-1)^2\}$, here $\beta = 4{\cdot}865 \times 10^{-11}$ and v is the frequency of vibration of the tom, is shown to agree well with the observations down to 23° bsolute when the values of v observed optically by Rubens and Hollnagel are used. The example of diamond is especially interesting, because both theory and observation indicate that its specific eat becomes practically zero at so high a temperature as 42° bsolute.

The physical interpretation of the equation above given is discussed some length.

The possible application of the equation in the exact determination atomic weights is also pointed out. As an example the atomic eight of silver is calculated from the specific heat-temperature curve be 107·55.

T. E.

Mean Specific Heat of Crystallised and Fused Silicates 20—100°. KARL SCHULZ (*Centr. Min.*, 1911, 632—640).—The llowing determinations were made in a water calorimeter with the icate heated at about 100°, and the water at about 20°. The assy materials were obtained by fusing the crystallised silicates an electric oven.

	Crystallised.	Amorphous.
Lead metasilicate ($PbSiO_3$)	0·07807	0·07886
Adularia from St. Gotthard	0·1855	0·1895
Microcline with albite from Arendal	0·1865	0·1919
,, ,, ,, ,, Miask	0·1845	0·1884
,, ,, ,, ,, Sætersdalen	0·1878	0·1909
Spodumene* from Branchville, Conn.	0·2161	0·2176

* M. p. about 1380°.

In every instance the specific heat is greater for the amorphous terial than for the corresponding crystallised material. L. J. S.

Phosphoryl Chloride as a Cryoscopic Solvent. GIUSEPPE ODDO and ANNA MANNESSIER (*Gazzetta*, 1911, **41**, ii, 212—223. Compare Walden, Abstr., 1910, ii, 1036).—Phosphoryl chloride, m. p. about $-1°$, containing some hydrate, has a cryoscopic constant 70·2 (compare Oddo, Abstr., 1901, ii, 492). By fractional distillation over phosphoric oxide and repeated fractional crystallisation the melting point can be raised to 1·37°. The higher values given by Besson and by Thorpe must be erroneous, and the values $-1·78°$ and $+1·782°$, attributed to Oddo by various writers, including Walden (*loc. cit.*), were never obtained by him. Phosphoryl chloride of the highest melting point cannot be kept. For cryoscopic purposes, purification by dehydration, distillation, and a few crystallisations is sufficient; it then has m. p. 0·4—0·9°, and the cryoscopic constant of this product is 72·1. This constant was obtained from experiments with acetic anhydride, *n*-propyl ether, acetone, *n*-hexane, cyclohexanone, and sulphur chloride. Determinations with aromatic substances gave much more widely varying numbers, owing to substitution, and the mean was considerably higher. Hence the value 76·8, found by Walden, must be considered too high. The latent heat of fusion of phosphoryl chloride (calculated from $K = 72·1$), is 20·9 cal. R. V. S.

Cryoscopy in Fused Sodium Thiosulphate. A. BOUTARIC (*Compt. rend.*, 1911, **153**, 876—877).—The freezing point of the salt $Na_2S_2O_3,5H_2O$ is 48·5°, and the temperature at which the solid pentahydrate and dihydrate are in equilibrium with the liquid is 48·2°. When the fused pentahydrate is employed as solvent for carbamide, sucrose or sodium chlorate, nitrate or sulphate, the molecular lowering of the freezing point is 44°. For potassium chlorate, nitrate, chloride and sulphate, and for ammonium nitrate, the lowering is practically double this number, corresponding with almost complete ionisation of these salts. W. O. W.

Cryoscopic Behaviour of Quaternary Aromatic Ammonium Salts in Bromoform, and the Cryoscopic Measurement of a Velocity of Decomposition. EDGAR WEDEKIND and F. PASCHKE (*Ber.*, 1911, **44**, 3072—3080. Compare Abstr., 1910, ii, 597).—From cryoscopic measurements it is found that quaternary ammonium salts of the type $CH_2Ph{\cdot}NMePhRX$ (where R = methyl, propyl, isobutyl or allyl, and X = Br or I) are considerably associated in bromoform solution, the association factor being approximately 2. The association cannot be attributed to the residual affinity of an unsaturated element, since it is found that phenylbenzylmethylallylammonium *d*-camphorsulphonate also exists in the form of double molecules.

The velocity of decomposition of phenylbenzylmethylallylammonium bromide in bromoform solution has been determined by measuring the gradual alteration in the depression of the freezing point. The initial constants thus obtained are in agreement with those determined by the polarimetric method.

Further evidence of the decomposition of quaternary ammonium

salts is furnished by the gradual diminution in the electrical conductivity of their solutions in chloroform; thus, after one hundred and fifty minutes at 25°, a 1·2% solution of phenylbenzylmethylallylammonium iodide has a specific conductivity of only two-thirds of the initial value.
F. B.

Volatility of Sulphur Compounds. MARCEL DELÉPINE (*Compt. rend.*, 1911, **153**, 725—727).—From collected data on the boiling point of numerous organic oxygen compounds and their sulphur analogues, it is shown that generally speaking substitution of sulphur for oxygen raises the boiling point, except in the case of water and the lower alcohols, phenols, and acids.
W. O. W.

Internal Pressure of Liquids and the Determination of the Absolute Zero. ÉMILE H. AMAGAT (*Compt. rend.*, 1911, **153**, 851—857. Compare Abstr., 1909, ii, 549).—Leduc has recently stated (this vol., ii, 792) that the internal pressure of a gas diminishes with rise of temperature, but calculations from Chappuis' data leave this open to doubt, especially when it is borne in mind that the values are referred to a hydrogen thermometer instead of to one containing a perfect gas.

Leduc's conclusion is necessary to the maintenance of the theory that the internal pressure for gases of the same molecular complexity is proportional to the square of their molecular weights. When the value of the function $T.dp/dt - p$ is calculated for hydrogen, it is necessary to pre-suppose the existence of a much greater variation of the internal pressure coefficient than can possibly exist, in order to bring the case into harmony with the theory. The values agree more closely with the present author's law of volumes when 273·0° is taken as the absolute zero than when the zero is taken as 273·1°. Conversely, assuming the truth of this law (that π and π', the components of internal pressure, vary inversely as the square of the volume for molecular distances sufficiently great), calculation of the absolute zero gives 272·983° as the absolute zero for hydrogen, and 272·999° and 272·996° for nitrogen and oxygen respectively. It is shown that the critical density of diatomic and triatomic gases increases regularly with the critical pressures in such a way that the ratio p/d^2 varies within somewhat narrow limits.
W. O. W.

Boiling Point of Water. EARL OF BERKELEY and MALCOLM P. APPLEBEY (*Proc. Roy. Soc.*, 1911, *A*, **85**, 477—489).—The boiling point of water, as determined by Buchanan's method (the so-called Landsberger-Sakurai method), has been compared with the hypsometer point. The small temperature differences involved were measured electrically by means of two platinum resistance thermometers. The sensitiveness of the measuring apparatus was such that the error attaching to the determination of the temperature difference was not more than 0·0001°.

The temperature at which water boils when a current of steam is passed through it depends on several factors, of which the chief are

the height of the liquid and the rate of passage of the vapour bubbles.

As compared with the hypsometric temperature, the boiling point rises with the height of the liquid if the steam is passed through at a constant rate. When the temperature differences are plotted against the height of the column of water, hyperbolic curves are obtained which cut the temperature axis at the origin at an approximate right angle. The curves can be represented by an equation of the form $t = kah^2/(h+\beta)$, in which t is the temperature difference, h the height of liquid, k, a, and β constants which depend on the form of the apparatus and the rate of bubbling.

For a given height of liquid, the boiling point falls with increase in the rate of passage of the steam. This apparently anomalous result is attributed to the influence of (1) the increased rate of bubbling on the agitation of the liquid, leading to increased loss of heat at the surface, and (2) the coalescence of the bubbles, leading to a diminished rate of heating. H. M. D.

Boiling Points of Some Saturated Aqueous Solutions. EARL OF BERKELEY and MALCOLM P. APPLEBEY (*Proc. Roy. Soc.*, 1911, *A*, **85**, 489—505. Compare Abstr., 1904, ii, 648).—The electrical temperature-measuring apparatus employed in the experiments with water (preceding abstract) has been applied to the accurate determination of the boiling points of saturated salt solutions according to Buchanan's method.

Since the effect of changes in barometric pressure on the temperature equilibrium is greater for saturated solutions than for water, boiling-point measurements were made at different pressures, and a barometer-coefficient determined for each salt. This coefficient, which represents the excess of the effect of a pressure of one millimetre of mercury on the temperature of the boiling saturated solutions over that on the hypsometer temperature, is dependent on the solubility of the salt and on the temperature-coefficient of the solubility. For sodium sulphate its value is 0·00052°, whilst for potassium nitrate the coefficient is 0·0217°.

From the hyperbolic curves which express the relationship between the boiling point and the height of the column of boiling salt solutions, boiling points corresponding with a very thin layer of solution are calculated by suitable methods of extrapolation. These values are then corrected by means of the corresponding barometer-coefficients, and in this way boiling points obtained for normal pressure.

The boiling-point data are applied to the calculation of osmotic pressures by means of Porter's equation; the values so obtained show that all the salts are dissociated with the possible exception of thallous nitrate. Data representing the composition and density of saturated solutions of strontium nitrate are given in an appendix. H. M. D.

Partial Pressures of Water and Alcohols in Aqueous Alcohols. V. ANTONY G. DOROSCHEWSKY (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 962—973. Compare Zawidzki, Abstr., 1901, ii, 6; Vrevsky, Abstr., 1910, ii, 1038).—By means of experimental data

obtained by Regnault, Konowaloff, and Vrevsky, the author deduces the two following theorems:

(1) In any aqueous alcoholic solution, the ratio between the partial pressures of the water at any two temperatures is equal to the ratio between the vapour pressures of pure water at these temperatures, or the change of the partial pressure of water with temperature is identical in all mixtures of alcohol and water, independent of the composition of the solution or of the nature of the alcohol.

(2) The ratio between the partial pressures of an alcohol in its aqueous solution at any two temperatures is identical for all solutions, and is identical with the ratio of the vapour pressures of the pure alcohol at the same two temperatures.

It is shown that the differences between the compositions of the vapours evolved from one and the same aqueous alcohol solution at different temperatures are a direct consequence of these two theorems. If P and p denote the vapour pressures of the alcohol and water at the temperature t, and P_1 and p_1 the corresponding magnitudes at t', then, if the ratio P/P_1 is greater than p/p_1, the increase of the partial pressure with rise of temperature is greater for the alcohol than for water. The values of this ratio for water and for various alcohols in the case of various pairs of temperatures are given in the following table:

	20°/30°.	30°/40°.	40°/50°.	50°/60°.	70°/80°.	80°/90°.	90°/100°.
Water	0·540	0·574	0·597	0·618	0·638	0·657	0·691
Methyl alcohol......	0·592	0·613	0·634	0·656	—	—	—
Ethyl ,, ...	0·564	0·585	0·607	0·628	0·647	0·662	—
Propyl ,, ...	0·517	0·546	0·597	0·599	0·623	0·647	0·691

It follows that with rise of temperature the vapours from aqueous methyl and ethyl alcohols become richer in water, whilst with aqueous propyl alcohol the opposite is the case. T. H. P.

Condensation of Vapours. FELIX BECKER (*Zeitsch. physikal. Chem.*, 1911, **78**, 39—70).—The phenomena attending the condensation of vapours which are in equilibrium with the crystalline form as stable phase have been investigated. The condensation was effected in the usual way by sudden adiabatic expansion, and the formation of fog was detected by a very sensitive method depending on the reflection and refraction of light by the particles. The substances chiefly used were nitrophenol, menthol, camphene, camphor, borneol, *iso*borneol, benzophenone, and iodine.

Substances which in the liquid form can be considerably supercooled condense at first as liquid drops, but substances which cannot easily be supercooled in the liquid form pass directly from vapour to crystalline form. The amount of reduction of pressure which is just sufficient to produce condensation on adiabatic expansion, and its dependence on the temperature, have been investigated, and it is shown that the condensation of a vapour to liquid drops occurs the more readily the denser the vapour, whereas the formation of crystals is retarded by increasing density of vapour. From the minimum depressions just sufficient to produce condensation, the supercooling which the vapours have undergone is determined, and hence a curve is constructed

showing the limits within which the vapour can be realised on crossing the sublimation curve.

Iodine is exceptional, inasmuch as on considerable reduction of pressure it condenses as visible particles, but with smaller depressions (as shown by thermal observations) it condenses as invisible particles. None of the other substances investigated shows an intermediate stage in condensation.

The supercooling before condensation occurs is the same whether the vapour is or is not in contact with a smooth glass wall, and hence the latter has no influence on the condensation.

Water vapour condenses as liquid drops for temperatures down to -[illegible] and reductions of pressures up to 400 mm., so that the limit ice-liquid lies at still greater reductions of pressure. G. S.

Pressure-Temperature Sections. J. P. WHITE (*Zeitsch. physikal. Chem.*, 1911, **78**, 71—85).—A space figure is constructed for a two-component system for the case in which the components form a solid compound which as regards volatility lies between the two components, the assumptions being that the components are completely miscible in the liquid state and not miscible in the solid state, and that the volatility of the liquid mixtures diminishes continuously according to the proportion of one of the components. By means of this figure and the simple space figure of Roozeboom, the pressure-temperature sections for varying conditions are completely investigated. G. S.

New Methods of Resolving Mixtures of Liquids with Adjacent Boiling Points or Constant-boiling Mixtures. A. GOLODTZ (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1041—1060).—The method used by the author consists in adding to the mixture of two liquids a suitable proportion of a third component which forms with one of the original constituents a constant-boiling mixture with a boiling point lower than those of all the other elements of the mixture, that is, of the liquids themselves, and of any other possible combinations; the ternary mixture thus obtained is then rectified. This method can be applied either when the boiling points of the two liquids are very close, or when they form a mixture with a constant boiling point.

Several examples are given, one which is of technical importance being as follows: If 195 grams of 65·5% aqueous acetic acid are mixed with 272 grams of toluene, and the mixture distilled through a Hempel column, the first fraction of 337 grams, b. p. 84—85·5°, will contain practically all the toluene and water and only 4·1% of the acid; the last fractions, amounting to 107 grams, contain 96·01% of acetic acid, and the final one of these, 64 grams, 99·9% of acid. T. H. P.

A Simplified Combustion Calorimeter. ROBERT WRIGHT (*Chem. News*, 1911, **104**, 201—202).—The calorimeter consists of a glass bell-jar carrying on its flange a lead weight heavy enough to sink the jar when filled with oxygen. The fuel is contained in a nickel crucible supported on a small tripod, which is part of the brass base

plate. This base plate is cut from heavy sheet brass, and provided with broad tongues at the edge to clamp it to the base of the jar; tongues are also cut in it which turn up and form the tripod.

The oxygen for combustion is led through a tube of Jena glass, which slides through a cork in the neck of the jar, and is enlarged at the lower end. The outside of the jar is fitted with a ring of brass wire gauze projecting at right angles to the sides.

The combustion is carried out in the usual way with calorimeters of this type, the factor of the instrument being found by burning a substance of known calorific value. T. S. P.

Thermochemical Investigations. IV. Heats of Combustion of Terpenes and Styrenes and Prediction of Heats of Combustion. KARL AUWERS, WALTER A. ROTH, and FRITZ EISENLOHR (*Annalen*, 1911, **385**, 102—116. Compare Abstr., 1910, ii, 586). —It has been found that the heats of combustion of the terpenes and the styrenes already published (*loc. cit.*) are about 0·5% too low, in consequence of the difficulty of ensuring the complete combustion of slightly volatile liquids in the bomb calorimeter. A new series of estimations, performed in a modified apparatus, is being carried out. The results, which show that the theoretical deductions stated previously are still correct, were being held back until the series was completed. However, the appearance of Lemoult's paper (this vol., ii, 583) forces an immediate answer from the authors. Lemoult's heats of combustion of styrene, α-methylstyrene, and $\alpha\beta$-dimethylstyrene differ from those obtained by the authors by a constant amount, about 1·2%. This suggests that the discrepancy is due to a constant error (probably in the value of the water-equivalent of the calorimeter). The confidence with which Lemoult relies on his experimental values on account of their agreement with "calculated" values may be misplaced, because, although in some cases the observed and the calculated values are concordant, in others the difference is more than 1%, that is, more than ten times the experimental error. C. S.

Vapour Pressure and Integral Heat of Solution for Saturated Solutions. ALEXANDER SPERANSKI (*Zeitsch. physikal. Chem.*, 1911, **78**, 86—109. Compare Abstr., 1909, ii, 378).—The differences in the vapour pressures of pure solvent and saturated solution have been determined by the tensimeter for saturated solutions of oxalic acid, succinic acid, and a number of inorganic salts in water, and for saturated solutions of acetanilide in chloroform, and m-dinitrobenzene in benzene and in chloroform, and from the results, the vapour pressures of the saturated solutions between 20° and 60° have been calculated. Except in the case of sodium thiosulphate, the vapour pressures increase as the temperature rises. In accordance with the principles of thermodynamics, the ratio p_1/p_2, where p_1 is the vapour pressure of the solution and p_2 that of the solvent, diminishes with rise of temperature, except for the solution of sodium carbonate monohydrate.

For all the solutions, the relationship between vapour pressure and temperature is satisfactorily represented by Bertrand's formula:

$p = k[(T-\lambda)/T]^n$, where k and λ are constants. From the analogy between vaporisation and dissolution, it might be anticipated that Bertrand's formula in the form $C = G[(T-\lambda)/T]^p$, where C is the solubility, would represent the variation of the solubility with temperature, and this is shown to be the case. The formula $\log p = a \log C + b$, where C is the solubility in grams per 100 grams of solution, and a and b are constants, is valid for most of the solutions investigated.

It is further shown that the formula $\log p_2/p_1 = a + b/T$ is valid for certain solutions, a and b being constants. Combining this with the formula $[d \log p_2/p_1]/dT = l/RT^2$ (Kirchhoff's formula), where l is the integral heat of solution, it follows that l must be nearly constant, and hence that the van't Hoff formula $\log (p_1/p_2) = -l/2T$ can be used to calculate the integral heat of solution for saturated solutions at temperatures exceeding 30—40°. G. S.

Dependence of the Integral Heat of Solution on the Temperature. A. WOITASCHEWSKY (*Zeitsch. physikal. Chem.*, 1911, **78**, 110—122. Compare Speranski, preceding abstract).—It is shown that all the formulæ representing the variation of the vapour pressure of a pure liquid with the temperature also apply to the variation of the vapour pressure of a saturated solution with temperature. On this basis, the conclusion is drawn that the integral heat of solution diminishes with the temperature when it is positive, and increases with temperature when it is negative; in other words, the absolute magnitude of the integral heat of solution always diminishes with the temperature. Kirchhoff's formula (compare Speranski, previous abstract) is not directly applicable to the experimental data. G. S.

The Theory of Solution and Heats of Dissolution. ALBERT COLSON (*Compt. rend.*, 1911, **153**, 812—814).—The author points out that the heat of dissolution of a gas should be equal to the sum of its latent heat of vaporisation and the heat of polymerisation of the dissolved molecule. This is known to be true in cases such as that of acetic acid, in which the degree of polymerisation is the same for the dissolved substance as when it is in the gaseous condition. The term *dissolecule* is employed to denote a polymerised molecule in solution. W. O. W.

A General Relation between the Physical Properties of Substances; Application to Densities. G. TER-GAZARIAN (*Compt. rend.*, 1911, **153**, 871—874. Compare Abstr., 1908, ii, 666; 1909, ii, 551).—It has been shown previously that for members of a homologous series, the densities corresponding with temperatures distant the same number of degrees from the critical temperature differ only by a factor which increases with the molecular weight and varies according to the series. It has now been found that this holds good, not only for densities, but also for coefficients of viscosity, heights of capillary ascension, rectilinear diameters, and the latent heat of vaporisation calculated by Mills' method. The best published data were employed for the verification of this generalisation. W. O. W.

Weight of a Falling Drop and the Laws of Tate. X Drop Weights of Some Further Associated and Non-associated Liquids, and the Surface Tensions and Capillary Constants Calculated from Them. J. LIVINGSTON R. MORGAN and F. T. OWEN (*J. Amer. Chem. Soc.*, 1911, **33**, 1713—1727. Compare Abstr., 1908, ii, 356, 668; this vol., ii, 372, 584, 585, 698, 699, 857).—On applying the equation $w(M/d)^{2/3} = k_B(t_c - t_0 - 6)$ to the drop weights in order to find a value of t_c independently of the temperature of observation and using in all cases the value of k_B found for benzene ($t_c = 288·5°$), it has been found that methyl hexyl ketone, phenylacetonitrile, benzaldehyde, piperidine, diisoamyl, isoamyl acetate, and nitrobenzene have a normal molecular weight, whilst methyl ethyl ketone, diethyl ketone, propionitrile, and acetone are abnormal and therefore associated.

The values of the surface tensions of these liquids in dynes, γ, and of the capillary constant, a^2, calculated respectively from the drop weights and drop volumes, agree well with the values obtained from the capillary rise.

Equations are given expressing the variation of the surface tension and the capillary constant, as found from the drop weight, for all the liquids mentioned. E. G.

The Viscosity of Suspensions and the Determination of Avogadro's Number. M. BANCELIN (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 154—156).—Measurements have been made of the viscosity of aqueous suspensions of gamboge and gum mastic. The experimental data are in accord with Einstein's formula, according to which the ratio between the viscosity of the suspension and the suspending medium is independent of the size of the suspended particles, but varies in a linear manner with the mass of the particles contained in unit volume of the suspension.

Experiments with various aqueous solutions indicate that the relationship between the viscosity of the solution and of the solvent can be represented in certain cases by a formula of the same type. This is true for solutions of glycerol, sucrose, and sulphuric acid, but not for solutions of phenol or carbamide.

The validity of Einstein's viscosity formula for suspensions of molecular dimensions permits of the deduction of the number of molecules in unit volume. From the data for sucrose solutions this is found to be 70×10^{22}, which agrees satisfactorily with Perrin's value deduced from observations on the Brownian movement.

H. M. D.

Molecular Complexity in the Liquid State. PHILIPPE A. GUYE (*J. Chim. phys.*, 1911, **9**, 505—518. Compare Turner and Merry, Trans., 1910, **97**, 2069).—Association in the liquid state was held by Turner and Merry to be due to electrical rather than chemical forces. The author is unable to find any essential difference between the two points of view, since chemical forces are almost certainly electrical in origin. Moreover, polymerisation in the liquid state is related to polymerisation in the vapour by the mass action law (Abstr.,

1910, ii, 841). Surface tension, boiling point, vapour tension, and latent heat measurements do not indicate the molecular complexity of liquids apart from the surface film, and where easily oxidisable substances, such as phenylurethane and diphenylamine, are measured in contact with air the result may be wholly misleading. All the liquids giving higher values of Ramsay and Shields' coefficient than $k=2.1$ are substances of high molecular weight and high boiling point, and in these cases the high surface pressure may considerably influence the molecular condition in the surface film. The only trustworthy methods are those such as Traube's volume method, which is independent of the surface film.

The recent observations of Walden on tristearin, tripalmitin, and *iso*butyl ricinolate are to be interpreted as showing marked dissociation of these substances in the surface film. The author suggests that the dissociation products are alkylene and acid. R. J. C.

Stability of Oil-Water Emulsions. EMIL HATSCHEK (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 159—164).—The author discusses the conditions which determine the stability of emulsions and the rate at which clearing takes place under the influence of electrolytes. It is calculated that an emulsion of an oil of density 0·7, which contains 0·1% of the disperse phase and consists of particles of diameter $0·4\mu$, is subjected to an upward force amounting to $1·10^{-11}$ dyne per particle, whereas according to Lewis's data for the magnitude of the electric charge, the electrical force of repulsion between two neighbouring particles amounts to $2·3\times10^{-8}$ dyne. The very much greater magnitude of the electric force is in harmony with the exceptional stability of such highly disperse emulsions.

In accordance with Stokes's formula, the rate of clearing of particles of a given size on the addition of an electrolyte must depend to a large extent on the difference between the densities of the disperse phase and the dispersive medium. In this connexion, observations are recorded relating to the condition of oil-water emulsions at intervals of twenty-four, forty-eight, and one hundred and twenty hours after the addition of an electrolyte. The clearing process involves three stages: (1) the electric discharge of the particles; (2) the formation of larger complexes; (3) the mechanical separation of these from the dispersive medium, and of these, the second and the third represent changes which in general require considerable time for their completion. H. M. D.

The Nature of Solvates and the Relationships between Adsorption and Dissociation. WOLFGANG OSTWALD (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 189—195).—The view is put forward that solvates may be regarded as absorption compounds between solute and solvent. For the special case of aqueous solutions of salts, reference is made to the connexion between the ionisation of a given salt and its degree of hydration, and it is pointed out that Noyes's formula $C(1-\gamma)=K(C\gamma)^r$ connecting the degree of ionisation (γ) with the concentration (C) can be written in the form $C\gamma=K_2(C-C\gamma)^n$, which is of the same type as the adsorption formula $x=K(C-x)^n$.

Not only is the form of the equations identical, but more or less quantitative relationships are also shown to exist between the two groups of phenomena. The exponents in the two equations are of the same order of magnitude, and their variation is confined to rather narrow limits. Both ionisation and adsorption exhibit maxima, have small negative temperature-coefficients, and show similar deviations from the exponential formula at high concentrations. These facts are in favour of the hypothesis that the hydration of salts in aqueous solution may be looked on as an adsorption of the solvent by the solute.

H. M. D.

Adsorption of Neutral Salts. HILARY LACHS and LEONOR MICHAELIS (*Zeitsch. Elektrochem.*, 1911, 17, 917—919).—The statement in the previous paper (this vol., ii, 190) that the anion and cation are adsorbed in equivalent amount by blood charcoal from a neutral aqueous solution of potassium chloride is erroneous. As a matter of fact Cl' ions only, and no K˙ ions, are adsorbed. It would therefore be anticipated that the solution, after adsorption of Cl' ions, must contain free potassium hydroxide, but it has not been possible to obtain a quantitative proof of the presence of alkali. It is probable that the potassium is present as carbonate or other salt the negative component of which originates from impurities in the charcoal.

From an acidified solution of potassium chloride no K˙ ions are adsorbed, but in the presence of bases, such as ammonia and piperidine, K˙ is adsorbed. The adsorption of K˙ is most favoured when the solution is about $N/50$ with reference to ammonia. On the other hand, pyridine has no influence on the adsorption of K˙, so that the effect of bases depends partly on the nature of the cation. As it has previously been shown that Cl' ions are not adsorbed from an alkaline solution of potassium chloride, the potassium must be taken up as the hydroxide.

The authors consider that these observations support their view that adsorption in such cases is a purely electrical phenomenon.

G. S.

Adsorption Compounds (Van Bemmelen). UGO PRATOLONGO (*Gazzetta*, 1911, 41, ii, 382—412).—The author has carried out three series of experiments with the products which are precipitated when a solution of sodium aluminate is added to a solution of sodium silicate. The first series had for its object the determination of the variation in the composition of the precipitates formed, according to the relative concentrations of the solutions. The second set deals with the variation in the solubility of one of the compounds (of sodium aluminate and sodium silicate), according to the amount of the solid substance present. In the third series of experiments, determinations are made of the variations in the amount of ammonium chloride or potassium chloride adsorbed by the product used in the second series, according to the relative amounts of liquid and solid phases present. In these experiments the adsorption is measured by means of the equilibria

reached (*a*) when the concentrations of the salt solutions is increasing, and (*b*) when the concentrations of the salt solutions is decreasing. The results indicate that a solid phase of the type employed can give rise to a trivariant system, in which the solid phase behaves as though it had a variable concentration.

The system also presents the phenomenon of chemical hysteresis (evidenced in the third set of experiments), that is to say, permanent modifications may be formed. R. V. S.

Adsorption in Solution. I. Retention of Acids by Sheep's Wool. GEORG VON GEORGIEVICS and ARTUR POLLAK (*Monatsh.*, 1911, 32, 655—675).—The wool used was very carefully purified by treatment in turn with boiling distilled water, hot soap solution, boiling 2% hydrochloric acid (on the weight of wool), lukewarm very dilute ammonium carbonate, warm water containing very little acetic acid, and boiling distilled water.

The retention of acids by wool is an adsorption phenomenon which within certain limits takes place according to definite laws. In general, mineral acids are more strongly adsorbed than fatty acids. The concentration of the acid has considerable influence on the adsorption; an acid may be adsorbed more strongly than another acid from dilute solution and less strongly in more concentrated solution. There is no proportionality between the strength of an acid and its adsorption by wool; this is contrary to the conclusions of Walker and Appleyard with silk (Trans., 1896, 69, 1334). There is absolutely no connexion between the adsorption and the amount of dissociation of an acid.

Less acid is adsorbed by wool from a mixture of acids than the arithmetical mean of the adsorption from two acids used singly. This negatives the possibility of simple salt formation between the acid and the thread substance. E. F. A.

Substantive Dyeing. W. G. SAPOSCHNIKOFF (*Zeitsch. physikal. Chem.*, 1911, 78, 209—227).—Both the dyes and the materials were carefully purified, and, in contrast to the technical method, no salts were added. The dyeing was effected by boiling the material with a solution of the dye for two hours, a reflux condenser being used. The material was then washed, and the amount of dye taken up determined by fusing it with sodium hydroxide and nitrate, and estimating the sulphur as sulphate, the amount of sulphur in each dye being determined in like manner. The results of five series of experiments, in each of which the conditions were widely varied, are quoted.

It is shown that the results are represented satisfactorily by the adsorption formula: $\log C_f = \log\beta + 1/a.\log C_b$, where C_f and C_b are the final concentrations of dye in the material and in the bath respectively, and a and β are constants, or by the related formula: $C_f^2 + AC_f - A.10k = 0$, where A is a constant and $10k$ represents the dyeing limit, the greatest concentration of dye which the material can remove from the bath. A comparison of two experiments, for which all the characteristics are different, leads to the formula: $C_b/C'_b = [(10k - C_f)K'_w]/[(10k' - C'_f).K_w]$, that is, the end concentrations

of the baths are directly proportional to the differences between the dyeing limit and the effective dyeing, and inversely proportional to the bath moduli, which are functions of the original dye concentration in the bath.

The above laws are followed whether the materials retain their natural structure (cotton wool) or have undergone treatment (mercerised cotton). Under equivalent conditions mercerised cotton becomes dyed about 10% more deeply than the natural wool.

G. S.

Dissociation Constant K_2 of Sulphuric Acid and Oxalic Acid. JOHANNES E. ENKLAAR (*Chem. Weekblad*, 1911, **8**, 824—829).—By means of the hydrogen electrode and a dilute solution of sodium hydrogen sulphate, the author has determined the mean value of the second dissociation constant of sulphuric acid at 18° to be $K_2 = 0.018$. For oxalic acid the value K_2 was calculated from the dissociation curve of oxalic acid, and the concentration of the hydrogen ions (1.5×10^{-3}) in a solution containing 0·05 gram of sodium hydrogen oxalate per litre, and was found to be $K_2 = 4.7 \times 10^{-5}$. Another calculation based on the electric conductivity yielded the value $K_2 = 1.3 \times 10^{-5}$. Both the values obtained for oxalic acid are therefore of the same order as the dissociation constant of acetic acid, $K = 1.8 \times 10^{-5}$.

A. J. W.

Osmotic Pressure. MAURICE PRUD'HOMME (*Bull. Soc. chim.*, 1911, [iv], **9**, 857—862).—A mathematical investigation of osmotic pressure on the basis of an analogy between gravitational attraction and osmotic pressure. The details are unsuitable for abstraction. It is shown (1) that osmotic pressure is not directly proportional to the mass of the dissolved substance, which is in harmony with Fouard's experimental results; (2) that from the general equation arrived at in this investigation the known formulæ expressing the behaviour of dilute solutions under various conditions are deducible.

T. A. H.

The Theory of Solutions. ALBERT COLSON (*Compt. rend.*, 1911, **153**, 719—721).—The author considers that the experimental data on osmotic pressure are not sufficiently in agreement with theory to support the hypothesis as to the analogy between osmotic and gaseous pressure, that is, to warrant the identification of R and ρ in the expression $PV = RT$, and $\omega V = \rho T$ when ω is the osmotic pressure.

W. O. W.

Osmotic Measurements of Salt Solutions and Arrhenius' Theory of Ions. EUGÈNE FOUARD (*Compt. rend.*, 1911, **153**, 769—772. Compare this vol., ii, 267).—A theoretical discussion based on measurements of osmotic pressure made by the apparatus already described. The author draws attention to the divergences between his results and those required by the ionic theory.

W. O. W.

Direct Measurements of the Osmotic Pressure of Caseinogen in Alkaline Solution. Experimental Proof that Apparent Impermeability of a Membrane to Ions is Not due to the Properties of the Membrane but to the Colloid contained within the Membrane. BENJAMIN MOORE, HERBERT E. ROAF, and ARTHUR WEBSTER (*Biochem. J.*, 1911, 6, 110—121. Compare Moore and Roaf, Abstr., 1908, ii, 204).—The osmometer used in the experiments has been described in previous papers. At the commencement of an experiment, the osmometer chamber contained a certain concentration of caseinogen and of sodium hydroxide, and the outer liquid was a solution of sodium hydroxide of the same concentration as that inside the cell. The observed osmotic pressure was very low at first, but the exterior sodium hydroxide slowly diffused inwards through the membrane, and simultaneously the osmotic pressure increased. The inward passage of sodium hydroxide is against the gradient of osmotic pressure. The alkali in the osmometer unites in some form with the colloid, and it is this union which causes the osmotic pressure. The purpose of the membrane is the purely mechanical one of holding together the colloidal aggregates, and its apparent impermeability to the ions is quite fictitious. Free ions pass through quite readily, but ions associated with colloid are retained on the colloid side and produce pressure. The high concentration of crystalloid within and the low concentration without is due to a specific affinity between crystalloid and colloid. The maximum of osmotic pressure per 1% of colloid is reached at about 0·047*N* of free alkali, and further increase of alkali lowers osmotic pressure. In the course of the experiments pressures as high as 686 mm. were observed.

These considerations are applied to the elucidation of the osmotic behaviour of living cells, which is discussed in detail. G. S.

Permeability of Porcelain and Copper Ferrocyanide Membranes. F. E. BARTELL (*J. Physical Chem.*, 1911, 15, 659—674. Compare Bigelow and Bartell, Abstr., 1909, ii, 979).—The rate at which water passes through unglazed porcelain and through an electrolytic copper ferrocyanide membrane under the influence of pressures up to 5885·7 mm. and 2957·9 mm. respectively was found to obey Poiseuille's laws relating to capillary tubes.

The porcelain membranes gradually became less permeable during the experiments, apparently owing to fine particles being torn off and forced into the capillary passages. On this account each series of determinations was immediately repeated in reverse order, and the average of each pair of values at the same pressure was taken as the rate for the membrane half way through the experiment. The permeability of the copper ferrocyanide membrane deposited in porcelain was only about 4% of the permeability of the 4·5 mm. porcelain plate, and no clogging of the membrane occurred.

The rate of permeation varied directly as the pressure at a constant temperature, and inversely as the viscosity of water when the temperature was altered and the pressure kept constant.

The fact that the same laws govern the passage of water through capillary tubes as through porcelain and ferrocyanide membranes is not

...ssarily in favour of the theory that these membranes are capillary structure, since the passage of liquids through molecular interstices ...y be found to be amenable to the same mathematical treatment.

R. J. C.

The Influence of Affinity in Solutions. MICHAEL RÓZSA (...itsch. Elektrochem., 1911, 17, 934—938).—When to a mixed solvent ... the components A and B a third substance, C, readily soluble in A ...t only slightly soluble in B, is added, the freezing point of the mixed ...lvent is very often raised. For example, the addition of water to the ...ixed solvent benzene-alcohol raises the freezing point of the latter to ... extent depending on the proportion of water added. The explana...n given is that C forms chemical compounds with A or B, the ...mber of molecules of solute being thus diminished. In this way the ...istence of molecular compounds of alcohol-water, phenol-water, ...ohol-glycerol, alcohol-lactic acid, phenyl-glycerol, phenol-lactic acid, ...ter-sulphuric acid, and water-stannous chloride has been proved. ...e quantitative composition of these compounds has not been ...termined.

The results appear to show the existence of considerable affinity ...tween solvent and solute in dilute solution, and also that the ...fluence of the solute extends over the whole of the solvent.

G. S.

Solubility of Sparingly Soluble Salts. MAURICE PRUD'HOMME (...J. Chim. phys., 1911, 9, 517—537. Compare Kohlrausch, Abstr., ...08, ii, 814).—The molecular conductivity, Λ, of a solution is ...proximately related to the dilution by the expression $\Lambda = cv^{1/n}$, ...ere c and n are constants. The minimum value, V, of the dilution for which ionisation is complete can be calculated, the ultimate ...lecular conductivity being represented by Λ_V instead of the more ...al Λ_∞.

It follows that $\Lambda_V - \Lambda_v = (V/v)^{1/n}$, where v is the dilution of a ...urated solution. The author shows that with twenty-one common ...valent salts n has a value very near 3·06. Taking $(\Lambda_V - \Lambda_v)/\Lambda_V = r$ ...d $1/\Lambda_V = R$, the above equation may be written $rv^{1/3 \cdot 06} = RV^{1/3 \cdot 06} = k$. ...e value of k deduced from Berkeley's accurate data for thallium ...oride is 0·40154. From these equations it is possible to deduce ... solubility of a salt, knowing the conductivity of its saturated ...ution and the value of Λ_V obtained from Kohlrausch's tabulated ...ues of the ionic conductivities.

...he solubilities of a number of sparingly soluble sulphates, ...bonates, oxalates, etc., deduced in this way agree very well with ... solubilities calculated by Kohlrausch in the majority of cases, ... when the salts are hydrated, the author's method gives too high a ...e for Λ_∞, and hence too low a value for the solubility.

...ith the very sparingly soluble salts cuprous thiocyanate, mercuric ...de, lead chromate, silver bromide, and silver iodide, the dilution in ...rated solution is higher than that required to give complete ...ation, that is, $v > V$. The author's solubility values are then to be ...erred to those of Kohlrausch. In all cases where $V > v$ the

empirical formula $v = 0{\cdot}904 \times (\Lambda_{\infty} = 1/10^{3}\chi)^{1\cdot}$ may be used to calculate the solubility. This equation is independent of the conception expressed by V, and requires only the determination of the conductivity of the saturated solution. R. J. C.

Effect of Salts on the Solubility of Other Salts. I. ARTHUR A. NOYES and WILLIAM C. BRAY (*J. Amer. Chem. Soc.*, 1911, 33, 1643—1649).—The well-known solubility principles, based on the law of mass-action, that (1) the product of the concentrations of the ions of a salt, present as solid phase, has the same value in dilute solutions of other salts as it has when present alone, and that (2) the concentration of the non-ionised portion of a salt, present as solid phase, has the same value in dilute solutions of other salts as it has when present alone, are not accurate, but are subject to deviations, those of the first lying in the opposite direction to those of the second. The work described in this and the following papers has been undertaken with the object of studying the character and magnitude of these deviations, and, for this purpose, the concentration of the non-ionised portion and the product of the concentrations of the ions of the salt with which a solution is saturated have been calculated.

It is shown by reference to curves in which the solubilities of lead chloride, thallous oxalate, silver sulphate, and calcium hydroxide are plotted against the concentration of added salts, namely, lead nitrate, potassium oxalate, potassium sulphate, and sodium hydroxide respectively, that, in the case of uni-bivalent salts, the solubility-product principle is not even approximately true when a salt with a common bivalent ion is added. The ion-concentration product increases greatly, since the large addition of the bivalent ion is not compensated by any great decrease of the univalent ion of the salt with which the solution is saturated. E. G.

Effect of Salts on the Solubility of Other Salts. II. ARTHUR A. NOYES, C. R. BOGGS, F. S. FARRELL, and M. A. STEWART (*J. Amer. Chem. Soc.*, 1911, 33, 1650—1663. Compare preceding abstract).—Determinations have been made of the solubility of potassium perchlorate in presence of potassium chloride and potassium sulphate at 25°, of thallous chlorate and sulphate in presence of each other at 20°, and of thallous sulphate in presence of thallous nitrate, sodium sulphate, and sulphuric acid at 25°. Conductivity measurements were made in order to obtain the various ionisation values.

The results show that the solubility of potassium perchlorate is reduced by the presence of potassium chloride or sulphate. The chloride has less influence on the solubility than the sulphate, which corresponds with its lower degree of ionisation.

The solubilities of thallous chlorate and sulphate are reduced when both salts are present as solid phases.

The solubility of thallous sulphate is greatly diminished in presence of thallous nitrate, a salt with a common univalent ion, and the decrease agrees qualitatively with the principle of the constancy of the ionic solubility product. Sodium sulphate, on the other hand, does not effect the expected reduction, the solubility being lessened by

... in a 0·1*N*-solution of this salt, and is actually increased by ... *N*-solution. The solubility is also increased by sodium hydrogen ...ate and by sulphuric acid. E. G.

...ect of Salts on the Solubility of Other Salts. III. ...ubility of Thallous Chloride in Solutions of Potassium ...trate, Potassium Sulphate, and Thallous Sulphate at 25°. ...iam C. Bray and W. J. Winninghoff (*J. Amer. Chem. Soc.*, ..., 33, 1663—1672. Compare preceding abstracts).—Experiments ...een made to ascertain the effect of thallous sulphate and of ...assium nitrate and sulphate on the solubility of thallous chloride. ...se are supplementary to the work of Noyes (Abstr., 1892, 1143) ...the solubility of thallous chloride in presence of thallous nitrate, ...ous chlorate, and several chlorides. The solubility and conductivity ...asurements were made at 25°.

The solubility of thallous chloride is increased by the presence of ...assium nitrate or sulphate, salts without a common ion, as would ...expected on account of the formation of thallous nitrate and ...phate by metathesis. The solubility is greatly decreased by ...ous sulphate, a salt with a common ion, and this decrease is in ...itative agreement with the principle of the constancy of the ...solubility product. The solubility curves for salts with a ...mon ion seem to lie more closely together than would be expected ...m the widely different ionisation values. E. G.

Effect of Salts on the Solubility of Other Salts. IV. ...antitative Discussion of the Solubility of Uni-univ...ent Salts in the Presence of Other Salts. William C. ...ay (*J. Amer. Chem. Soc.*, 1911, 33, 1673—1686. Compare preced...g abstracts).—The results of the work recorded in the two preceding ...pers are discussed quantitatively by a method which consists essen...ly in calculating, by the aid of the ionisation values, the concen...tion of the non-ionised portion and the product of the concentrations ...the ions of the salt with which the solution is saturated, both when ...s present alone and when another salt is present.

According to the mass law, the concentration (BA) of the non-ionised ...tion and the solubility product $(B^+)(A^-)$ should be constant in ...y saturated solution. It is shown, however, that in every case the ...mer decreases considerably and the latter increases slightly as the ...al concentrations of the salts and of the ions in the saturated ...tion increase.

These variations can be expressed approximately as a function of ...e total ion concentration (Σi) in the solution by the exponential ...ations $(BA) = k_u(\Sigma i)^{m_u}$ and $(B^+)(A^-) = k_i(\Sigma i)^{m_i}$, in which k_u, k_i, ... and m_i are constants which were separately determined for each ...stance in the presence of each added salt. In the case of thallous ...oride, in which the range of concentration of the added salts was ...y large, the equations do not fully express the results, but different ...ues of m_i or m_u must be assumed at different concentrations. The ...ues found for these exponents are recorded. Those for m_i at the

concentration 0·016*N* are small and less than those ... concentrations, and this indicates that the solubility product ... practically constant in the case of less soluble salts in ... small quantities of other salts.

The values of m_i are much smaller than those of m_u at ... trations, and hence the deviation from the theoretical ... $(B^+)(A^-)/(BA) = k$ is due more to abnormal behaviour ... ionised substance than to abnormal behaviour of the ions.

These results indicate that the ratio of the activity (Lewis, Abstr., 1908, ii, 16) to the concentration of univalent ions is nearly ... below 0·016*N*, but that at higher concentrations it decreases ... increasing concentration, at first slowly and then more rapidly ... corresponding ratio for the non-ionised portion increases ... with increasing concentration throughout the whole range ... concentrations investigated.

The nearly uniform effect exerted on the concentration of ... ionised portion and on the solubility product by the salts ... different valence types, and by those with and without a common ... confirms the assumption that the ionisation relations of uni-univalent salts are primarily determined by the total equivalent ion-concentration. There are, however, consistent differences of secondary order ... effects of the different kinds of salts, and especially between uni-univalent and uni-bivalent types.

Laws of "Concentrated" Solutions. III. Ionisation and Hydration Relations of Electrolytes in Aqueous Solution at 0°: (A.) Cæsium Nitrate, Potassium Chloride, and Lithium Chloride. EDWARD W. WASHBURN and DUNCAN A. MACINNES (*J. Amer. Chem. Soc.*, 1911, 33, 1686—1713. Compare ... ii, 862).—Determinations have been made of the depression of f. p., densities, relative viscosities, and equivalent conductivities of solutions of cæsium nitrate, potassium chloride, and lithium chloride at 0°, and of concentrations up to *N* in the case of potassium and lithium chlorides, and to 0·5*N* in that of cæsium nitrate. ... salts were selected, since cæsium nitrate is only slightly or not at all hydrated, whilst lithium chloride combines with large quantities of the solvent, and potassium chloride occupies an intermediate position.

The cryohydric point for cæsium nitrate is −1·254°.

When the f.-p. curves for the three salts are compared with that of the normal solute, that is, one which is neither associated, dissociated, nor hydrated, potassium chloride is found to agree exactly up to about 0·5*N*, lithium chloride deviates decidedly in the direction of hydration, whilst cæsium nitrate deviates markedly in the opposite direction. The conclusion is drawn that deviation from the behaviour of a normal solute cannot serve as the basis for the calculation of the degree of hydration of an electrolyte. Another method for making this calculation is indicated, which has shown that about 9 mols. of water are combined with 1 mol. of potassium chloride, and about 18 mols. with one of lithium chloride in 0·5*N* solutions.

The f.-p. data for cæsium nitrate are compared with those of ...

Abstr., 1902, ii, 310), and his statement that this salt obeys the law of mass action cannot be entirely confirmed. E. G.

Ultramicroscopic Observation of a Temperature Coagulation. THE SVEDBERG and KATSUJI INOUYE (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 153—154).—The influence of temperature on the coagulation of colloidal solutions of platinum in ethyl ether has been investigated by means of the ultra-microscope. When the number of particles observable in the ultra-microscope is plotted as a function of the temperature, two straight lines are obtained indicating a sudden change at 28—29°. This critical temperature agrees with that found previously as the result of microscopic observations.

H. M. D.

The Coagulation and Gelatinisation of Silicic Acid. NICOLA PAPPADÀ (*Zeitsch. Chem. Ind. Kolloide*, 1911, 9, 164—175).—The influence of electrolytes and of sucrose, separately and conjointly, on the gelatinisation of colloidal solutions of silicic acid has been investigated, and in reference to these experiments the author discusses the mechanism of the gelatinisation process. The colloidal particles are supposed to consist of membranes having a capillary structure. In consequence of the negative charge on the particles, water cannot enter into the capillary network until means are provided for the removal of the charge. Neutralisation of the charge is effected in presence of electrolytes by the positive ions, and gelatinisation can then take place as a result of the intrusion of water. If non-electrolytes only are added to the colloidal solution, the osmotic forces are unable to bring about gelatinisation, because of the impermeability of the membranes so long as the particles are electrically charged.

Experiments have also been made on the coagulation of silicic acid by colloidal ferric hydroxide. Quantitative measurements show that the oppositely charged colloids are precipitated in approximately constant proportions, excess of either remaining unchanged in the colloidal condition. The quantitative proportions appear to be related to the valencies of silicon and iron. H. M. D.

Application of the New Theory of Allotropy to the System Sulphur. ANDREAS SMITS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 263—270).—As in the case of acetaldehyde, it is shown that the relationships exhibited by the equilibria between the different forms of sulphur can be accounted for if it is assumed that sulphur represents a pseudo-ternary system. H. M. D.

Phenomena of Condensation for Mixtures of Carbonic Acid and Nitrobenzene in Connexion with Double Retrograde Condensation. PHILIPP KOHNSTAMM and J. CHR. REEDERS (*Proc. K. Akad. Wetensch. Amsterdam*, 1911, 14, 270—278).—The influence of nitrobenzene on the condensation of carbon dioxide has been examined, and data are recorded which show the pressures characteristic of the three-phase systems at different temperatures in the neighbourhood of the liquid-liquid plait points. H. M. D.

Thermal Analysis of Quaternary Systems. II [illegible] PARRAVANO and G. SIROVICH (*Atti R. Accad. Lincei*, 19[illegible] ii, 331—337. Compare this vol., ii, 973).—A mathematical [illegible] the problem of constructing the diagram of a quaternary [illegible] the study of plane sections taken through a vertex of the [illegible] and parallel to an edge. R. [illegible]

Calculation of Equilibrium Constants from Cry[illegible] Measurements. J. B. GOEBEL (*Zeitsch. physikal. Chem.* [illegible] 244—254).—The method described in the previous paper (A., 1910, ii, 268) is extended to solutions of binary and ternary [illegible] lytes in which polymerisation occurs. For the deduct[illegible] numerous equations, the original paper must be consulted. [illegible] examples of binary electrolytes, organic acids are chosen, [illegible] case of acetic acid the concentration of double and triple [illegible] aqueous solution is calculated. As an example of a ternary [illegible] sodium sulphate is chosen. The value of $k = C_1^2/C_2$, where C_1 [illegible] sents simple Na_2SO_4 molecules and C_2 double molecules, [illegible] is shown in the last case that the molecular conductivities [illegible] calculated from the formulæ. [illegible]

Basicity of the Organic Acids Containing Alc[illegible] Hydroxyl Groups. G. CALCAGNI and LUIGI BERNARDINI [illegible] *Accad. Lincei*, 1911, [v], 20, ii, 261—267, 309—312).—The [illegible] have investigated the influence of alcoholic hydroxyl groups [illegible] basicity of organic acids, the experimental method adopted [illegible] measurement of the conductivity of solutions of the acids [illegible] different dilutions) during gradual neutralisation with a weak [illegible] (ammonia). The acids examined were glycollic, lactic, [illegible] butyric, hydroxy*iso*butyric, malic, tartaric, and citric acids, [illegible] results are given in the form of tables and in curves, in which [illegible] ordinates are the specific conductivities and the abscissæ the [illegible] tions of ammonia present. The curves of neutralisation first [illegible] through a minimum, then rise until neutralisation is complete, [illegible] afterwards run parallel to the axis of abscissæ. In the polybasic [illegible] the pauses corresponding with the neutralisation of the individual [illegible] carboxyl groups are not prominent. On the whole, the influence [illegible] the hydroxyl groups does not show itself at all in the curves, but [illegible] may be due to the considerable dilutions employed. All the [illegible] dealt with can be titrated very well with phenolphthalein and potassium hydroxide. R. V. S.

The Alkalinity of Aqueous Solutions of Carbonates. FRIEDRICH AUERBACH and HANS PICK (*Arbeit. K. Gesundheitsa[illegible]* 1911, 38, 243—274).—The alkalinity of aqueous solutions of sodium carbonate, sodium hydrogen carbonate, and mixtures of these salts in different proportions has been determined at 18° by a colorimetric method in which the colour effects produced by addition of various indicators are compared with the colours exhibited by standard solutions of known hydrogen ion concentration.

From the data thus obtained, the second ionisation constant of

carbonic acid, $k_2 = [H^{\cdot}][CO_3'']/[HCO_3']$, is found to be $6 \cdot 0 \times 10^{-11}$. This is in agreement with McCoy's value (Abstr., 1903, ii, 413), and also with that yielded by the data of Shields (Abstr., 1893, ii, 418) and Knoblauch (Abstr., 1900, ii, 395). The divergent constants given by the two latter authors are due to errors of calculation.

From the above constant, the degree of hydrolysis of sodium carbonate solutions of different concentration has been calculated. The hydrolysis of sodium hydrogen carbonate solutions is nearly independent of the concentration, and corresponds with $[OH'] = 0 \cdot 0015$ at 18° and 0·0025 at 25°, the concentration being expressed in millimols per litre. In contrast with the large temperature coefficient indicated by these numbers, the degree of hydrolysis of sodium carbonate varies very little between 18° and 25°. H. M. D.

Velocities of Reaction of Acetone and Lutidone with Phenylhydrazine and Hydroxylamine Under Various Conditions. Iwan Schöttle (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1180—1194).—The author's experiments were made in aqueous solutions at 16—18°, the concentrations of the ketone and phenylhydrazine (or hydroxylamine) being decinormal.

The progressive addition of small quantities of hydrochloric acid produces a continuous diminution in the velocity of interaction of acetone and phenylhydrazine.

Acetic acid first produces a very considerable fall in the velocity of this reaction, but as the proportion of the acid is increased, the velocity also increases until it attains approximately the original value in 100% acetic acid.

It has been found by Thiele and Schneider (Abstr., 1909, i, 929) that unsaturated cyclic ketones, similar in structure to lutidone, do not form phenylhydrazones, but combine with the phenylhydrazine. The author, however, confirms the statement of Petrenko-Kritschenko and Mosseschwili (Abstr., 1902, i, 190) that lutidone gives a phenylhydrazone.

The formation of lutidonephenylhydrazone is accelerated by hydrochloric acid, but in presence of acetic acid (10% or 40%) the velocity of the reaction is zero.

The interaction of acetone and hydroxylamine is retarded by sulphuric acid, but hastened by potassium hydroxide. The latter completely suppresses the reaction of ketones with phenylhydrazine. The velocity of reaction of lutidone with hydroxylamine is zero under all conditions (compare Petrenko-Kritschenko, and Stamoglu, Abstr., 1903, i, 197). T. H. P.

Case of Autocatalysis and Simultaneous Negative Catalysis. Antonio Quartaroli (*Gazzetta*, 1911, **41**, ii, 64—69. Compare this vol., ii, 1086).—The reaction between nitrates and anhydrous formic acid is a process of autocatalysis in which nitrogen trioxide is the positive catalyst. Until a trace of this substance has been formed, the velocity of the reaction is very small, but the nitrogen trioxide cannot accumulate in quantity, because it also reacts with formic acid. In agreement with this view it is found that oxidising

agents, transforming the nitrogen trioxide into nitric acid ... negative catalysts. Traces of potassium chlorate, hydrogen ... potassium permanganate, or carbamide hinder the reaction or ... entirely, so that there results the paradox that oxidising ... may prevent oxidation (compare Ihle, Abstr., 1896, ii, 460 ...

R. V. S.

Catalytic Esterification of Dibasic Acids in the Wet Way. JEAN B. SENDERENS and J. ABOULENC (*Compt. rend.*, 1911, 153, 881—884. Compare this vol., ii, 600, 637).—By ... mixture of malonic acid (1 mol.) and alcohol (2 mols.) with ... its volume of sulphuric acid for an hour, the amount of ester ... is 67·5%, or 82·4% if twice the amount of alcohol is used. The ... not increased by using 10% of sulphuric acid, but 5% of ... aluminium sulphate or potassium hydrogen sulphate may ... stituted for the acid without impairing the result. In practice ... yield is less, owing to the solubility of the ester in the washing ... but this loss is not so serious with the higher alcohols; thus ... alcohol (4 mols.) gave an actual yield of 75·4%, and isoamyl ... (4 mols.) 85·6% of ester. With succinic or oxalic acid and ... alcohol under the same conditions, the yields were practically the ... In the case of phthalic acid, it is necessary to employ 15% of ... acid to obtain good results. W. O. W.

Atomic Weights of the Dominant Elements. GUSTAVUS D. HINRICHS (*Compt. rend.*, 1911, 153, 817—818. Compare Abstr., 1893, ii, 317; 1907, ii, 945).—The author has previously elaborated ... method for the simultaneous calculation of the atomic weights of ... of the elements engaged in a particular reaction, and has published ... résumé of over 1000 results derived from 340 reactions used ... accurate atomic-weight determinations (Abstr., 1909, ii, 653). ... are now classified according to their limits of precision. The ... class consists of those determinations of the highest accuracy in which the maximum difference between the experimental and absolute values does not exceed 0·012; this comprises 454 values distributed among ten elements (O, Cl, Ag, C, Na, S, Br, H, Na, K). These are ... the dominant elements, and in the author's opinion their true atomic weights are identical with their absolute atomic weights, the latter being whole numbers. W. O. W.

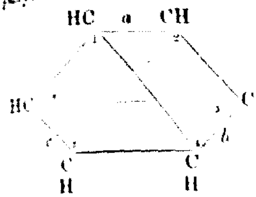
The Cyclic Molecule. A New Hypothesis on Benzene, Allotropy and Polymerism. ANÍBAL CHACÓN (*Pamphlet*, pp. 15) —A theoretical paper in which a new hypothesis is put forward as to the constitution of benzene. The author gives the formula (I) for benzene, the molecule of which he considers as consisting of three "sub-nuclei" (*a*, *b*, *c*), corresponding with three molecules of acetylene, which mutually saturate one another.

In his formula the author considers that the *ortho*-position is 1:6, the *meta*-position 1:3 or 1:5, and the *para*-position 1:2. By his hypothesis he explains the fact of two isomeric benzene hexachlorides, assigning to them formulæ II and III for *a* and *β* respectively.

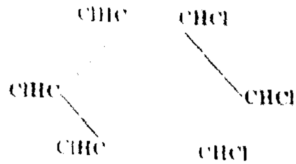
He then proceeds to give structural formulæ for naphthalene,

anthracene, and phenanthrene, and for heterocyclic compounds, such as pyridine, the pyrone derivatives, etc.

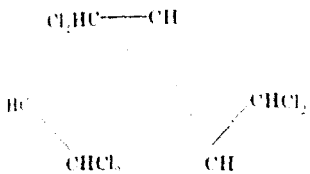
Finally, he deals with allotropy and polymerism, explaining the polymerism of cyanic acid into cyanuric acid, and of cyanogen into



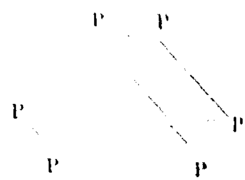
(I.)



(II.)



(III.)



(IV.)

para-cyanogen by the formation of cyclic molecules. He explains the allotropy of oxygen, sulphur, phosphorus, etc., on the same lines, giving, for example, for red phosphorus formula IV.

Finally, he enunciates the following conclusions:

(1) A simple substance can exist in two or more states, differing from one another by the number of atoms which the molecule contains in each of the states.

(2) Certain compounds are capable of giving rise to other compounds, the molecules of which are formed by two or more primitive molecules mutually saturating one another, this saturation being produced by pre-existing unsaturated valencies, or, if saturated, by alteration in the direction of the valencies.

(3) The atoms or molecules of elements and the molecules of compounds mutually saturate one another in the cyclic form, when they are assembled to the number of three, to constitute an allotropic or polymeric molecule. W. G.

A New Funnel. II. PHILIP BLACKMAN (*Chem. News*, 1911, **104**, 211).—The funnel previously described (this vol., ii, 796) is further improved by rounding off the bends (for example, where the neck of the funnel connects with the upper part) instead of having them sharp. T. S. P.

A Funnel Support. II. PHILIP BLACKMAN (*Chem. News*, 1911, **104**, 211).—The funnel support previously described (this vol., ii, 796) is better made of aluminium and not of glass. T. S. P.

Simple Apparatus for Filtering under Increased Pressure. ALFRED LOHMANN (*Zeitsch. Biol.*, 1911, **57**, 183—184).—The

apparatus consists of a strong cast iron vessel provided with a removable lid, which can be firmly fixed and through which a tube passes connected to a cylinder of compressed gas. In the lower part of the vessel is placed a filter plate, and the vessel narrows to a tube from which the filtrate can be drawn off. The pressure in the upper part of the vessel can be increased until the desired rate of filtration is obtained. F. F. A.

Apparatus for Extraction at High Temperatures. R. SCHURAVLEFF (*J. Russ. Phys. Chem. Soc.*, 1911, **43**, 1189—11..).—On an annular expansion on the outside and near the top of a ... extractor rests a narrow glass bell, mouth downwards. Steam is supplied to a perforated annular tube placed beneath the mouth of the bell, into which the steam rises and thus heats the extracting ... If the latter requires a higher temperature than is thus attained, the steam may be superheated, whilst if a lower temperature is desired, a portion of the steam is diverted by means of a three-way cock ... steam-delivery tube. In order that the condensed steam may not find its way into the flask containing the extracting liquid, round the ... tube of the extractor is fitted a slightly conical, rubber disk which carries the water off to one side. T. H. P.

Inorganic Chemistry.

Formation of Hydrogen Peroxide in the Electrical Discharge. ADOLPHE BESSON (*Compt. rend.*, 1911, **153**, 877—8..).—Kornbaum's results (Abstr., 1910, ii, 818) are considered inconclusive and might be attributed to formation of ozone or oxides of nitrogen. A more rigorous examination of the production of atmospheric hydrogen peroxide has been undertaken, employing conditions of temperature and pressure analogous to those obtaining in the higher regions of the atmosphere, and using a very dilute solution of potassium chromate, which is a specific reagent for hydrogen peroxide. Negative results were obtained on passing the silent electrical discharge through water vapour alone, below 0° and at 30—760 mm. In presence of oxygen, however, the production of hydrogen peroxide is very marked, but only at 385—770 mm. In presence of air, the results are less decisive, owing to formation of oxides of nitrogen which destroy the hydrogen peroxide. Nevertheless, the formation of this substance has been detected when the air was in large excess and in rapid circulation. W. O. W.

Synthesis of Concentrated Hydrogen Peroxide by means of the Silent Electrical Discharge. FRANZ FISCHER and MAX WOLF (*Ber.*, 1911, **44**, 2956—2965).—The authors describe a special apparatus by means of which oxy-hydrogen gas can be submitted to a silent electrical discharge, the gas pressure being maintained at 3 cm. of mercury. The discharge passes through a U-tube, which is cooled by liquid air. Under these conditions a yield of 2·25—2·56% of the total possible hydrogen peroxide was obtained, the yield being calculated on the quantity of oxy-hydrogen gas passed through the

U-tube. No hydrogen peroxide was formed when the U-tube was only cooled to − 20°.

The pressure of 3 cm. was chosen, because the gaseous mixture is not then explosive. The next experiments were made at the ordinary pressure, in one case the gaseous mixture consisting of 3% hydrogen and 97% oxygen; in the other case, of 3% oxygen and 97% hydrogen. In the former case, ozone was alone produced, and in the latter case the percentage yield of hydrogen peroxide varied with the temperature. At 22° it was 6·4%; at − 20°, 33·6—34·1%; at − 80°, 54%, and at the temperature of liquid air, 59—87·5%. In one case, the hydrogen peroxide solution produced was 86·9% by weight. In these experiments 500 c.c. of the mixture took 1·5—3 hours to pass through the discharging apparatus.

When a mixture of 1 vol. of oxy-hydrogen gas and 4 vols. of carbon dioxide was submitted to the discharge in a tube cooled by a mixture of ether and solid carbon dioxide, the yield of hydrogen peroxide was 4%.

The authors find that the limits of explosibility of mixtures of oxygen and hydrogen at the ordinary pressure are: 5·45% hydrogen and 94·55% oxygen; 5·3% oxygen and 94·7% hydrogen, the percentages being expressed in volumes. T. S. P.

Products Containing Absorbed Iodine. Lamberto Corridi (*Arch. Farm. sperm. Sci.*, 1911, 12, Reprint 13 pp.).—When animal charcoal is placed for twenty-four hours in solutions of iodine, this element is absorbed, and a certain amount is retained by the charcoal even after many hours at 120°. The charcoals prepared in this way contain (according to the solvent used) 1·87—7·50% of iodine, no trace of which is evolved on keeping. The iodine is slowly removed, however, by organic solvents for iodine, by water, dilute acid, and especially by dilute alkali and by animal tissues. Hence the iodine charcoal should be of service in medicine. R. V. S.

Formation of Ozone by Electrolysis with Alternating Current. Ebenezer H. Archibald and H. von Wartenberg (*Zeitsch. Elektrochem.*, 1911, 17, 812—816).—Dilute sulphuric acid is electrolysed in a cooled U-tube with platinum electrodes. The anode consists of a short platinum tube of 1 mm. diameter fused into glass tubes and cooled by the flow of water through it. An alternating current, the strength of which can be varied independently, is passed between the electrodes in addition to the direct current used for electrolysis. The effect of the superposition of the alternating current is to depolarise the electrodes. The anode potential falls rapidly as the ratio between the strengths of the alternating and direct currents increases up to about 3, and more slowly thereafter. With the anodic current density 1·5 ampere per sq. cm., for example, the anode potential was reduced by 3 volts when the ratio of alternating to direct current increased from 0 to 4. The increase in the strength of the alternating current is accompanied by an extraordinary increase in the quantity of ozone formed at the anode. A very small fraction of the ozone is produced by the alternating current alone. The higher the current density the smaller is the effect of the superposed alternating current. The strength of acid which gives the largest

quantities of ozone appears to diminish as the current density increases. The most favourable conditions observed were: area of anode 0·333 sq. cm.; direct current 0·25 ampere, alternating current 1·5 ampere, sulphuric acid of density 1·478. The ratio of ozone produced by direct current was 0·37, but owing to the large quantity of electrolytic gas produced by the alternating current the resulting gases only contained 0·23% of ozone. T. E.

Reversible Light Reaction of Sulphur. ALBERT WIGAND (*Zeitsch. physikal. Chem.*, 1911, 78, 208).—In a previous paper (this vol., ii, 878) the heat of formation of S_μ has been put equal to the alteration of the free energy by light. This is not strictly justifiable, but at present the data for accurate calculation of the free energy are not available. G. S.

A Simple Hydrogen Sulphide Apparatus. E. RATTENBURY HODGES (*Chem. News*, 1911, 104, 189).—The apparatus consists of two stout conical flasks fitted with rubber stoppers, and connected by a T-piece, one flask being inverted over the other; the projecting arm of the T is bent downwards. The top flask contains the iron sulphide resting on a wooden grid, previously soaked in paraffin wax, and the lower flask the acid. It is only necessary cautiously to invert the apparatus in order to get a flow of gas. W. G.

Industrial Preparation of Pure Nitrogen. GEORGES CLAUDE (*Compt. rend.*, 1911, 153, 764–766. Compare Abstr., 1906, ii, 1—).—The apparatus for the separation of air into oxygen and nitrogen, by a process of partial liquefaction and fractionation has been improved by arranging that the gaseous phase rich in nitrogen is liquefied in the colder liquid circulating at the base of the rectification column, instead of in the bath of oxygen. The liquid phase through which the gas passes then contains only 0·4% of oxygen, whilst the nitrogen escaping from the top of the column contains not more than 0·2% of oxygen, a degree of purity sufficient to meet the requirements of the cyanamide industry. W. O. W.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. I. Ammonolysis of Hydrazine Sulphate. ARTHUR W. BROWNE and T. W. B. WELSH (*J. Amer. Chem. Soc.*, 1911, 33, 1728—1734).—Franklin (Abstr., 1905, ii, 581) has drawn attention to certain reactions in which liquid ammonia acts in a manner analogous to that of water in hydrolysis, and for which he has therefore proposed the term "ammonolysis." Experiments have now been undertaken to investigate the behaviour of the nitrogen hydrides and their derivatives in liquid ammonia.

Hydrazine sulphate is decomposed by liquid ammonia at −33° in accordance with the equation: $N_2H_4,H_2SO_4 + 2NH_3 = (NH_4)_2SO_4 + N_2H_4$. The resulting solution of hydrazine in liquid ammonia may be decanted or filtered from the solid substance, which consists of ammonium sulphate or a compound of this salt with ammonia, and a method is thus suggested for the preparation of hydrazine from its sulphate.

It is shown that the same reaction takes place to a limited extent when hydrazine sulphate is submitted to the action of ammonia gas at the ordinary temperature. E. G.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. II. Ammonolysis of Certain Hydrazine Salts. ARTHUR W. BROWNE and A. E. HOULEHAN (*J. Amer. Chem. Soc.*, 1911, 33, 1734—1742. Compare preceding abstract).—The behaviour of hydrazine monosulphate, N_2H_4,H_2SO_4, and of hydrazine oxalate, diselenate, and mono- and di-phosphate in liquid ammonia has been investigated.

It has been found that the monosulphate, dioxalate, and diselenate are decomposed with formation of hydrazine and the corresponding ammonium salts, whilst the mono- and di-phosphate are not affected. When hydrazine monosulphate is treated with ammonia gas at the ordinary temperature, ammonolysis occurs to some extent, and a liquid, consisting essentially of a solution of hydrazine monosulphate in free hydrazine, can be separated from the mixture by centrifugal action. E. G.

Behaviour of the Hydronitrogens [Nitrogen Hydrides] and their Derivatives in Liquid Ammonia. III. Action of Ammonium Trinitride on Certain Metals. ARTHUR W. BROWNE and A. E. HOULEHAN (*J. Amer. Chem. Soc.*, 1911, 33, 1742—1752).—Ammonium trinitride can be prepared by passing dry ammonia into an ethereal solution of azoimide. When a solution of this salt in liquid ammonia is treated with lithium, sodium, potassium, calcium, or magnesium, vigorous action ensues with the formation of the respective trinitrides, and the liberation of ammonia and hydrogen in accordance with the equation: $M + NH_4N_3 = MN_3 + NH_3 + H$. In the case of zinc, aluminium, and tin, no perceptible action takes place, whilst with platinum a very slow reaction occurs.

A modified form of the Schiff nitrometer has been devised for use in this work, in which weighed quantities of two solids may be brought together in liquid ammonia in absence of air and moisture, and the gases evolved may be collected, measured, and preserved for subsequent analysis; this also permits of the residual solid being weighed and preserved, or prepared for analysis. E. G.

New Method for the Preparation of Nitrous Oxide and its Application to the Analysis of Nitrates. ANTONIO QUARTAROLI (*Gazzetta*, 1911, 41, ii, 53—59. Compare this vol., ii, 1079).—Nitrates react with pure, crystallisable formic acid quantitatively, according to the equation: $2KNO_3 + 6H{\cdot}CO_2H = N_2O + 4CO_2 + 5H_2O + 2H{\cdot}CO_2K$. The reaction affords a convenient mode of preparation for nitrous oxide, the gas evolved being collected over 20% potassium hydroxide solution at 40°. The gas is free from other oxides of nitrogen provided that the reaction is commenced by warming the mixture with a naked flame until the first bubbles appear. Gas is then rapidly evolved for some minutes without further heating. If the initial warming is gentle (for instance, in a water-bath at 25°), an intense

blue coloration appears, and red fumes are seen which are not produced when the warming is carried out quickly.

The method also permits of rapid and accurate estimation of nitrates, the procedure being as follows. In a test-tube provided with a gas delivery tube are placed 5 c.c. of formic acid and the weighed sample (about 0·2 gram) of nitrate. The reaction is commenced by sudden heating, as above described, and the gas is collected in a graduated vessel over mercury, a correction being applied for the air originally contained in the apparatus. From the volume of carbon dioxide and nitrogen, the percentage of nitrate can be estimated; the carbon dioxide is then absorbed by means of potassium hydroxide, and from the volume of nitrogen remaining, a second calculation is made as a check. The method has been tried for the nitrates of sodium, potassium, ammonium, calcium and lead, and experiments with chemically pure nitrates indicate an average error of about 0·3 in the nitrogen percentage found. It is recommended for the analysis of commercial sodium nitrate, the impurities in which do not affect the accuracy of the estimation. R. V. S.

Crystalline Form of Nitrogen Sulphide. G. F. Herbert Smith (*Min. Mag.*, 1911, **16**, 97—99).—Crystals of nitrogen sulphide, N_4S_4, prepared by F. P. Burt and F. L. Usher (Abstr., 1911, ii, [illegible]), gave constants [$a:b:c = 0·8879:1:0·8480$; $\beta = 89°37'$] in close agreement with those obtained by E. Artini (Abstr., 1906, ii, 533). The crystals are, however, of a different habit, having the appearance of cubes with truncated edges and corners. The refractive indices (about 2·046 and 1·908) are near to those of rhombic sulphur. L. J. S.

Oxidation of Arsenious and Antimonious Oxides. J. Bishop Tingle (*J. Amer. Chem. Soc.*, 1911, **33**, 1762—1763).—When arsenious oxide (0·5 gram) is boiled for twenty-six hours with 95% alcohol (3 c.c.) and water (5 c.c.), it is completely converted into arsenic acid. Antimonious oxide behaves in a similar manner. E. G.

Quantity of Carbon Dioxide in the Atmosphere at Monte Video. Johannes Schröder (*Chem. Zeit.*, 1911, **35**, 1211).—Ten thousand parts by volume of the air were found to contain from 2·[illegible] to 3·30 volumes of carbon dioxide, the average quantity being 2·[illegible] volumes. The largest quantities of carbon dioxide were found during June and July, 1908, and the smallest in February, 1909. The quantity tended to increase when the wind blew from the interior, and diminished during the sea breezes. W. P. S.

History of Colloidal Silicic Acid. Paul Walden (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 145—146. Compare Abstr., 1910, ii, 500).—A historical reference to the earliest observations on the solubility of silicic acid, and the behaviour of its solutions towards acids. Quotations are given from papers by Pott (1746), Baumé (1773), and reference made to the experiments of Meyer (1775-1785) and Bergman (from 1779 onwards). H. M. D.

Diffusion of Neon through Hot Quartz. OWEN W. RICHARDSON and R. C. DITTO (*Phil. Mag.*, 1911, [vi], 22, 704—706).—A new silica tube, which had never contained any foreign substance, was exhausted and heated in the air for about an hour at 1000°. The gas contained in the tube was then drawn off and examined. It gave a faint blue argon spectrum, and showed the yellow helium line. After three hours' heating, the helium spectrum was fully developed, and the neon line $\lambda = 5852$ was well marked. After being heated all night, the helium and neon spectra were both quite strong, but no sensible increase in the intensity of the argon spectrum could be detected.

From these experiments the author draws the conclusion that neon diffuses through quartz at about 1000°, but its coefficient of diffusion is smaller than that of helium. The first argon spectrum, which did not change in intensity with the time of heating, is attributed to traces of air absorbed by the walls of the tube before the heating commenced. H. M. D.

Volatilisation of Electrodes in a Tube of Neon. GEORGES CLAUDE (*Compt. rend.*, 1911, 153, 713—715. Compare this vol., ii, 602).—An account of experiments to explain the appearance of helium in luminescent tubes of neon apparently free from this gas. The tube employed was cross-shaped, and had four copper electrodes. The current was passed between two opposite electrodes until a sufficient amount of copper had volatilised, and then between the remaining pair.

It was found that the first deposit gave 1 c.c. per gram of gas rich in helium on treatment with nitric acid, whilst the second yielded a gas in which neon was the predominant constituent. It follows, therefore, that the results described in a previous communication cannot be ascribed to a transformation of neon into helium, but were probably due to a selective action of copper for helium, whereby a concentration of this gas was effected to a sufficient extent to enable it to be recognised spectroscopically. Ramsay and Collie have conducted experiments leading to the same conclusion (private communication). W. O. W.

Rare Gases of Coal Mine Natural Gases. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.*, 1911, 153, 847—849).—Analyses of five natural gases from mines are given. The amount of helium and neon varies between 0·0003 and 0·05%, and that of argon (with traces of krypton and xenon) from 0·003 to 0·04%, by volume. The relative proportions of the inert gases are about the same as in other natural gaseous mixtures. W. O. W.

Solidification of Aqueous Solutions of Metallic Chlorides. ALEXANDER W. SPERANSKY and A. PAVLINOVA (*J. Russ. Phys. Chem. Soc.*, 1911, 43, 1006—1022).—The authors have investigated the compositions of the crystals obtained on freezing solutions of sodium, potassium, calcium, and magnesium chlorides of varying concentration and containing different proportions of sodium hydroxide or hydro-

chloric acid (compare Roozeboom, "Die heterogenen Gleichgew... 2, 222; Balló, Abstr., 1910, i, 355).

With NaCl–HCl solutions, it is found that, in the more con... solutions, the ratio between the amounts of chlorine in ... of sodium chloride and hydrogen chloride respectively ... both for the solid separating and for the mother liquor. W... solutions, however, the value of this ratio is much greater f... than for the mother liquor. Similar relations are obser... NaCl–NaOH, KCl–HCl, and $CaCl_2$–HCl solutions.

With $MgCl_2$–HCl solutions, even when concentrated, the pres... of magnesium chloride in the ice is observed.

It was found, however, that the concentration has no ... influence, the principal part being played by the consistency ... separated ice, which is in hard masses from concentrated ... and in a friable condition from dilute solutions when slow... That this is the case was shown by cooling two solutions of ... composition in such manners that they gave the two kinds of ...

These phenomena are regarded as being due to adsorption ...

T. H. P.

Preparation of Lithium Persulphate. C. Nicolescu ... (*Zeitsch. Elektrochem.*, 1911, 17, 919).—The attempt was made ... prepare lithium persulphate by electrolysis of a solution of lithium sulphate in sulphuric acid at $-20°$, but although the persulphate was obtained in solution, it could not be separated in the solid form. An alternative method was therefore used. Persulphuric acid was prepared by electrolysis of sulphuric acid in the usual way, the sulphuric acid removed as the barium salt, lithium carbonate added to the persulphuric acid thus obtained, and the filtered solution evaporated in a vacuum. The pink, crystalline product contained about 8... of lithium persulphate, the remainder being lithium sulphate. The pure persulphate was not obtained.

G. S.

Preparation of Ammonium Salts from Nitrogen Compounds of Aluminium. Badische Anilin- & Soda-Fabrik (D.R.-P. 235...). —When aluminium nitride is heated with sulphuric acid (or aluminium sulphate) and water, the following reactions take place:

$$2AlN + H_2SO_4 + 6H_2O = 2Al(OH)_3 + (NH_4)_2SO_4$$
$$6AlN + Al_2(SO_4)_3 + 24H_2O = 8Al(OH)_3 + 3(NH_4)_2SO_4.$$

The products can be employed as manure, and the reaction has been extended to the production of ammonium acetate and nitrate by employing acetic acid or nitrous gases respectively in this operation.

F. M. G. M.

The Ternary System Zinc–Lead–Tin. Mario Levi-Malvano and O. Ceccarelli (*Gazzetta*, 1911, 41, ii, 269—282).—From the thermal study of numerous mixtures of zinc, lead, and tin, the authors have constructed the thermal diagram of this ternary system. The general form of the gap of miscibility resembles those given by Wright (1773), and ...son (Abstr., 1891, 267). The ternary eutectic separates at ... responds with a mixture of 5% of zinc, 24% of lead, and

... tin. **The alloys were also studied** microscopically, and ...graphs are given of the appearances presented. R. V. S.

Alloys of Zinc, Lead, and Tin. MARIO LEVI MALVANO and ...ANCELLI (*Gazzetta*, 1911, **41**, ii, 314—318). In view of the ...ance of alloys of these metals for industrial purposes, the ...ors have determined the hardness (with Brinell's apparatus, using ...essure of 500 kilograms) of the ninety-seven alloys prepared in the ...e of the work described in the preceding abstract. The results ...e recorded in a diagram, so that the connexion between hardness ...d composition can be seen, and it is pointed out that three alloys, ...h, according to Hiorns, are employed for anti-friction purposes, ...all in the area of alloys from which zinc crystallises first, but are ...ry near the zinc-lead eutectic, and microscopically consist of long ...ystals of zinc disseminated in a mass of the binary eutectic containing ...ttle of the tertiary eutectic. R. V. S.

The Alloys of Tellurium with Zinc. MATSUSUKE KOBAYASHI (*Mem. Coll. Sci. Eng. Kyôtô*, 1911, **3**, 217—220).—Tellurium and zinc ...m a single compound, TeZn, which melts at 1238·5°, and has D^{12} ...·4. The two eutectic points practically coincide with the pure ...ponents. The freezing-point curve falls steadily from the com...nd to tellurium, but alloys richer in zinc lose zinc so rapidly by ...atilisation that it is not possible to determine the course of the ...ve, although the zinc eutectic arrest is well marked. In ...roscopical examination the compound appears in needles.

C. H. D.

The Ternary System Copper Silver Gold. ERNST JÄNECKE (*Metallurgie*, 1911, **8**, 597—606). The freezing point of gold is ...pidly lowered by the addition of silver, and does not, as stated ...y Roberts-Austen and Rose (*Proc. Roy. Soc.*, 1903, **71**, 161), remain ...actically constant up to 50% Ag. The curve is a smooth one, ...ightly convex upwards, and the interval of crystallisation is ...ever more than 13°. The majority of the ternary alloys form ...mogeneous, solid solutions, the range within which duplex ...ructures are observed being defined by the eutectic line, which runs ...om the eutectic point of the copper-silver alloys at 60·2 atomic ...Ag and ends at a point corresponding with 42·5 atomic % Cu, ...5% Ag, and 24·0% Au, at a temperature of 800°. The curve ...eparating homogeneous and heterogeneous alloys passes through ...is point and through the limiting concentrations of the two ...pper-silver solid solutions. These results are confirmed by ...icroscopical examination. C. H. D.

The Corrosion of Metals. PERCY LONGMUIR (*J. Iron Steel Inst.*, ...11, **83**, 147—169).—A deposit obtained from the atmospheric ...rrosion of brass contained 22·75% ZnO, 15·93% CuO, 7% CO_2, and ...65% SO_3, whilst another sample, due to corrosion by fumes from ...uminating gas, contained 36·18% SO_3. Samples of iron rust, formed ...y purely atmospheric corrosion, contained from 0·686% to 3·124% SO_3. ...ust from steel rails, especially when laid in tunnels, also showed a

high proportion of sulphur. Corrosion by sulphuric a[illegible] brittleness in iron or steel.

Cerium-Tin Alloys. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1911, 72, 319—328).—Metallic cerium reacts with most gases [illegible] readily melted. If introduced into a carbon tube and heat[illegible] and nitride are formed, and the metal does not yield a r[illegible] throwing a piece of cerium (93·48% Ce) into a carbon tub[illegible] heated to 1200° without any protecting gas, fusion t[illegible] place and a homogeneous mass is obtained, giving a[illegible] freezing point of 830° (623°, Muthmann and Weiss). Th[illegible] tin are prepared in the same manner. The freezing-poin[illegible] with increasing amount of tin, reaching a maximum a[illegible] 30% Sn, corresponding with the compound Ce_2Sn. There [illegible] maximum at 1165° and 56% Sn, corresponding with the [illegible] Ce_2Sn_3, and a third at 1135° and 64% Sn, due to the comp[illegible] Microscopical examination is rendered difficult by the rap[illegible] of the sections, even when polished and examined under [illegible] but it is possible to recognise the compounds as homogen[illegible] detect the eutectic structure in other alloys of the serie[illegible] alloys containing less than 80% Sn are pyrophoric, espe[illegible] containing the compound Ce_2Sn, mere scratching with a ha[illegible] producing a shower of sparks. This compound has also the [illegible] hardness, of about 6, is very unstable in air, and rea[illegible] vigorously with water. C. H. D.

The Ferromagnetic Compounds of Manganese with Phosphorus, Arsenic, Antimony, and Bismuth. SIEG[illegible] HILPERT and THEODOR DIECKMANN (*Ber.*, 1911, 44, 2831—28[illegible]). *Manganese phosphide*, MnP, was prepared from mangan[illegible] phosphorus in a manner similar to that used for the arsenide [illegible] vol., ii, 985). It forms an inodorous, black powder, which b[illegible] heating in the air, giving magnetic, black oxidation products. It [illegible] insoluble in hydrochloric acid, which acid may therefore be used t[illegible] purify it; it is readily soluble in nitric acid.

Manganese antimonide, MnSb, was obtained by heating a mangan[illegible] amalgam, prepared by electrolysis, with the requisite amount [illegible] antimony in an atmosphere of hydrogen, the mercury being th[illegible] distilled off. It is a grey substance, which burns in the air, giv[illegible] non-magnetic products; it is soluble in hot hydrochloric acid [illegible] readily soluble in nitric acid. *Manganese bismuthide*, MnBi, [illegible] prepared similarly to the antimonide, and has similar chem[illegible] properties; it is silver-white in colour.

The following are the temperatures at which the magnetic pr[illegible] perties of these compounds are lost and regained, the first tempera[illegible] ture denoting loss of magnetic properties on heating, and the sec[illegible] gain of the same on cooling; they indicate that hysteresis occurs: MnP, 18—26°; MnAs, 40—45°; MnSb, 320—330°; MnBi, 360—[illegible] The higher the atomic weight of the element combined with mangane[illegible] the higher is the temperature at which the magnetic properties [illegible] lost. T. S. P.

The Thermal Formation of Potassium Manganate from Manganese Dioxide and Potassium Hydroxide. F. BAHR and ... SACKUR (*Zeitsch. anorg. Chem.*, 1911, 73, 101—124. Compare ... Abstr., 1910, ii, 214, 215; this vol., ii, 400; Askenasy and ..., Abstr., 1910, ii, 297).—The dissociation pressure of mixtures prepared by adding manganese dioxide to molten potassium hydroxide and pulverising the product have been measured. The dissociation pressure of manganese dioxide at 572° is 816 mm. From the curves thus obtained, an isothermal dissociation curve is drawn for the temperature 661°, and the results show that the final product of dissociation is potassium manganite, K_2MnO_3, which has no dissociation pressure, even at 1000°. Potassium manganate and manganite, however, form a solid solution, which is saturated when the atomic proportion of available oxygen to manganese is 1:1·6, corresponding with the composition $3K_2MnO_4,2K_2MnO_3$. The formation of products further saturated than this is attributed to supersaturation. This degree of oxygen corresponds with Sackur's compound $Mn_5O_{13},8K_2O$. C. H. D.

Cementation of Iron by Solid Carbon. GEORGES CHARPY and S. BONNEROT (*Compt. rend.*, 1911, 153, 671—673. Compare Abstr. ..., ii, 215).—Iron was heated in contact with graphite at 950° under very low pressures in an atmosphere of hydrogen, nitrogen, and carbon monoxide containing about one third of the latter. When the pressure did not exceed 0·3 mm., no cementation occurred. Cementation, however, was very distinct if the pressure was allowed to rise to 1—1·5 mm.; after thirteen hours' heating under these conditions the iron was found to contain 0·5% of carbon and to show the perlite structure. These experiments explain the contradictory results of previous observers, who have not taken sufficiently into account the effect of small quantities of carbon monoxide. W. O. W.

Iron Silicon-Carbon Alloys. W. GONTERMANN (*J. Iron Steel Inst.*, 1911, 83, 421—475).—The previous work on this system (Abstr., ..., ii, 851) has been extended. Increasing the percentage of silicon in cast iron accelerates the formation of graphite, but above 4—5% Si the temperature of reaction is so far lowered that the separation of graphite under ordinary conditions of cooling is diminished, becoming zero with more than 20% Si. C. H. D.

The Growth of Cast Irons after Repeated Heatings. HAROLD C. H. CARPENTER (*J. Iron Steel Inst.*, 1911, 83, 196—248).—The increase in external volume which takes place when cast iron is repeatedly heated in air is mainly due to disintegration caused by the oxidation of silico-ferrite. The distribution of the graphite affects the growth, by determining the access of oxidising gases. The presence of phosphide retards the oxidation. The higher the percentage of silicon in the iron, the greater the growth. When heated in a quartz tube in a vacuum, growth occurs owing to the escape of dissolved gases, and to a smaller extent, to the liberation of temper-carbon from carbide. An iron containing 3·98% of carbon and 1·07% of silicon shows a growth

of 11% under these conditions, and becomes porous and [illegible] crystalline. Increasing the silicon diminishes the growth in a [illegible] which becomes zero with 4% Si or more.

An alloy containing 2·66% C, 0·587% Si, and 1·61 [illegible] show growth after 150 heats. Its initial freezing point is [illegible]

C. H. [illegible]

The Influence of Vanadium on the Physical Pr[illegible] Cast Iron. William H. Hatfield (*J. Iron Steel In[illegible]*, [illegible] 318—331).—The addition of vanadium to cast iron fav[illegible] tion of the carbon in the combined condition, the greater part [illegible] vanadium entering into the carbide and increasing its stabil[illegible] 0·65% of vanadium, the carbide remains undecomposed afte[illegible] at 1040°.

C. H. [illegible]

Heat-treated 3% Nickel Steels. Andrew McWilliam a[illegible] J. Barnes (*J. Iron Steel Inst.*, 1911, **83**, 269—293).—The [illegible] point for steels containing 3% of nickel lies between 0·7[illegible] The point Ar_2 can be recognised as distinct from Ar_3 in [illegible] containing 0·12, 0·28, and 0·30% of carbon.

C. H. [illegible]

Influence of 0·2% Vanadium on Steels of Varying C[illegible] Content. Andrew McWilliam and Ernest J. Barnes (*J. I[illegible] Inst.*, 1911, **83**, 294—317). The pearlite point for steels [illegible] 0·2% of vanadium lies between 0·71 and 0·98% C. The p[illegible] is markedly irreversible, even in steels containing as little as [illegible] A part of the vanadium is in solid solution in the ferr[illegible]

C. H. [illegible]

The Chemical and Mechanical Relations of Iron, Chrom[illegible] and Carbon. John O. Arnold and Arthur A. Read (*J. Iro[illegible] Inst.*, 1911, **83**, 249—268).—A series of alloys, containing [illegible] 0·85% of carbon and variable quantities of chromium, have [illegible] examined. The ductility is increased by the addition of [illegible] chromium, and diminished by further additions up to 24 [illegible] carbides have been isolated by electrolysis in hydrochloric acid. [illegible] Practically the whole of the carbon in the annealed steels is [illegible] as carbides, the proportion of chromium in the carbide increas[illegible] at first with the proportion of chromium in the steel, afterwar[illegible] becoming constant. The constant product has the composit[illegible] $2Fe_3C,3Cr_4C$, and is probably a double compound, crystallis[illegible] slate-coloured needles. Alloys containing less than 5% of chrom[illegible] are pearlitic, whilst richer alloys consist of ferrite conta[illegible] chromium, with distinct particles of a double carbide. C. H. D.

The Influence of Impurities on the Corrosion of Iron. [illegible] W. Cobb (*J. Iron Steel Inst.*, 1911, **83**, 170—195).—When the [illegible] corrosion of iron is studied by means of the ferroxyl reagent (A[illegible] 1909, ii, 485) it is found that solution of the iron is greatly accelerate[illegible] by contact with ferrous silicate, black oxide scale, ferrous sulph[illegible] or iron phosphide or carbide. Graphite acts in the same manne[illegible]

Manganese sulphide is practically a non-conductor, and is without effect, and the behaviour of manganese silicate is similar. Manganese coupled with iron dissolves, the iron becoming the cathode. When two varieties of iron, such as Swedish steel and pure Swedish iron, are connected, any difference of potential between the two is found to be unimportant in comparison with the local currents, and corrosion takes place irregularly on both electrodes. When examined microscopically with the ferroxyl reagent, corrosion of ordinary iron is frequently found to begin at points where no recognisable impurity can be detected. These tests also show that manganese sulphide, like the silicate, does initiate local corrosion when present in microscopic particles. C. H. D.

I. The Cause of the De-rusting of Iron in Ferroconcrete. II. The Two Chemical Processes Occurring in a Railway Tunnel. Paul Rohland (*Zeitsch. angew. Chem.*, 1911, 24, 2011—2012).—I. A reply to Donath (this vol., ii, 897). The author rejects the explanation suggested by Michaelis, that the ferric oxide (rust) reacts with the lime of the concrete, forming a calcium ferrite, since he has not been able to detect any reaction between calcium hydroxide and ferric oxide, even after days.

II. In a railway tunnel at Hönebach it has been found that when lining it with cement or concrete the latter must be protected as long as possible from the action of sulphurous acid formed during the combustion of the coal burned on trains passing through. During the setting of the cement, calcium hydroxide is formed by hydrolysis, and this would combine with the sulphurous acid, ultimately forming calcium sulphate and bringing about the destruction of the cement.

The second chemical process referred to is the action of sulphurous acid on the old lime-mortar of the tunnel, whereby a plastic mass was formed, consisting of calcium sulphate and calcium hydrogen sulphate, the latter in the colloidal condition. T. S. P.

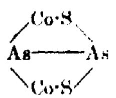
Ore Deposition in Relation to Iron Sulphides. Eugene T. Allen (*J. Washington Acad. Sci.*, 1911, 1, 170—177).—Iron pyrites and marcasite are produced artificially by the action of hydrogen sulphide on ferric sulphate solution, the latter being first reduced to ferrous sulphate with the separation of free sulphur ($FeSO_4 + H_2S + S = FeS_2 + H_2SO_4$). This reaction takes place at the ordinary temperature, and the dark precipitate is minutely crystalline; at a higher temperature (about 200°), in a sealed tube, distinct crystals are produced. Determinations of the relative amounts of iron pyrites and marcasite present in these products were made by the method of H. N. Stokes (Abstr., 1902, ii, 87); the results prove that higher temperatures and low degree of acidity favour the production of iron pyrites. At 100° in a solution containing 1% free sulphuric acid only marcasite is formed. Iron pyrites only is formed in neutral or alkaline solutions by the action of sodium polysulphide on a ferrous salt, or by the action of hydrogen sulphide on pyrrhotite and free sulphur. Marcasite when heated at 450° changes into iron-pyrites

with development of heat; but this change is not rever... iron-pyrites cannot be changed directly into marcasite. Pyrr... formed by the decomposition of iron-pyrites in hydrog... above 575°, more sulphur being lost at higher tempera... variable composition of pyrrhotite is explained by the solid ... sulphur in ferrous sulphide, the formula being $(FeS)_nS_x$.

The bearing of these experiments and temperature lim... cussed in connexion with the modes of occurrence in nat... minerals, their probable modes of origin, and the condit... for their formation. They are in harmony with the fact th... is formed near the surface from acid solutions, whilst ir... formed in deeper veins from hot alkaline solutions; pyrrh... other hand, often occurs in igneous and contact-metamorp...

L. J. S.

Experiments with Cobaltite. A. BEUTELL (*Centr. Min.*, 663—673).—Experiments were made on the same line... previously made with mispickel and glauc... vol., ii, 485, 728), the mineral being heated in a ... vacuum before and after roasting. Cobaltite w... to be more stable than glaucodote under these con... and the annexed constitutional formula is sugge...



The crystallised cobaltite from Håkansboda, Sweden, used ... experiments contained:

S.	As.	Fe.	Co.	Ni.	...
21·48	42·88	2·92	32·36	0·32	...

L. J. S.

Equilibrium between Chloropentamminocobalt Chloride and Aquopentamminocobalt Chloride in Aqueous Solution. P... PERS (*Compt. rend.*, 1911, **153**, 673—675).—The equilibrium be... purpureo- and roseo-cobalt chloride in aqueous solution has ... studied by boiling a solution of the former, and estimating the ... of the latter by precipitation as oxalate and the amount of precip... chloride by means of silver nitrate. The equilibrium curve ... reproduced, and show that two reactions occur simultaneously, ... corresponding with the equation:

$$(CoCl\cdot 5NH_3)Cl_2 + H_2O \rightleftharpoons (H_2O\cdot Co\cdot 5NH_3)Cl_3,$$

the other involving decomposition of both products with format... of cobalt chloride. If no decomposition occurred, equilibrium w... be attained when the mixture contained 42% of purpureo... chloride.

W. O. W.

The Exfoliation of Electrolytic Nickel. KARL ENGEM... (*Zeitsch. Elektrochem.*, 1911, **17**, 910—917).—Nickel electroly... deposited from an acidified solution of pure nickel chloride or sul... is obtained as a homogeneous coherent layer, whilst from amm... solution the metal is obtained in a form which peels off in shee... when no iron is present. When a solution of a nickel salt cont... iron is electrolysed, the iron deposits more easily than the nick... that the first layers are richer in iron than those deposited later, ...

owing to this inequality in composition, the metal tends to split off in thin sheets. The influence of various factors on the composition of the layers has been investigated. With increase of temperature, the proportion of iron in the different layers becomes more nearly equal, and the ratio of the total iron in the alloy to that in the solution diminishes.

The hardness of electrolytic nickel is very little influenced by the nature of the salt, whether sulphate or chloride; it increases with increasing acidity of the solution, and is diminished by the addition of sodium salts to the nickel solution.

The elasticity of the metal obtained from sulphate solutions is greater than that obtained from chloride solutions. The addition of sodium salts to the electrolyte also increases the elasticity. G. S.

Alloys of Nickel and Zinc. ÉMILE VIGOUROUX and A. BOURBON (*Bull. Soc. chim.*, 1911, [iv], 9, 873—879). Tafel has shown (Abstr., 1908, ii, 105), that nickel combines with zinc to form an alloy $NiZn_3$, and this has been confirmed by Voss (Abstr., 1908, ii, 194). The authors find that two alloys exist, $NiZn_4$ and Ni_3Zn.

The ingots obtained were homogeneous when the amount of nickel was below 19%, at this stage they became brittle, and when the amount of nickel was largely increased, they became cavernous, porous, and more and more malleable. They were not magnetic up to 70·9% of nickel, but became magnetic at 72·8% of this metal. When pulverised and subjected to the action of hydrochloric or acetic acid, the residues from mixtures containing up to 18·3% of nickel became progressively richer in this element and developed magnetic properties. The residues from mixtures containing over 18·3% nickel showed little variation in composition as the attack progressed. Alloys containing less than 18% of nickel on treatment with nitric acid (1%) gave invariably a residue containing 18·6% of nickel, corresponding with the alloy $NiZn_4$, which was isolated in this way as a crystalline, non-magnetic powder of density 7·71 and m. p. 850° (approx.). This was rapidly attacked by hydrochloric acid (1%), leaving a magnetic deposit which was sometimes pyrophoric; the solution generally contained zinc only. Dilute sulphuric acid attacked the alloy slowly, forming a solution of the two sulphates, and depositing a magnetic powder. Nitric acid of more than 1% strength dissolved the alloy completely. Nickel chloride solution dissolved the alloy on warming, giving rise to zinc hydroxide and a magnetic deposit.

Determination of the *E.M.F.*'s developed by the use of poles formed of mixtures of the two metals against poles of zinc showed "breaks" at 18·33% and 72·92% of nickel, corresponding with the compounds $NiZn_4$ and Ni_3Zn respectively. T. A. H.

The Reactions in a System of Nickel or Platinum, Mercury, and Sodium Chloride. CHARLES A. PETERS (*Amer. J. Sci.*, 1911, [iv], 32, 386—387).—When a solution of sodium chloride is left over mercury with a nickel wire connecting both liquids, crystalline nickelous hydroxide is formed very slowly, sodium hydroxide being produced at the same time. When platinum is substituted for nickel,

mercurous chloride is formed, sodium hydroxide be... produced.

Chromic Sulphates and Ions. ALBERT COLSON (... 1911, [iv], 9, 862—868. Compare Abstr., 1907, ii, 267, ...). The author has shown previously (*loc. cit.*) that sol... chromic sulphates give anomalous conductivity and cry... ments after heating and after dilution. To explain th... Recoura's suggestion that the violet sulphate undergoes p... and then hydrolysis, thus: $2Cr_2(SO_4)_3 + H_2O = [Cr_4O ...$ H_2SO_4, and on thermochemical evidence supposed that ... reaction occurred with the isomeric chromic sulphate ... has been called in question by Urbain as the result of ... work and that of Denham (Abstr., 1908, ii, 389). Th... suppose that when the violet sulphate is boiled, the polym...

$$[Cr_4(SO_4)_4]2SO_4,$$

is formed, and is more or less hydrolysed without therm... This explanation is improbable from what is known of poly... this composition (compare Recoura, Abstr., 1896, ii, 27...; ... Abstr., 1907, ii, 177). T. A. H.

Uranyl Salts. III. ALEXIS M. VASILIEFF (*J. Russ. Ph...* *Soc.*, 1911, 43, 1183—1184. Compare Abstr., 1910, ii, 107...). ... author has determined the values of n_D^{15} and D_{15}^{15} of a series of ... aqueous solutions containing from 54·77% to 2·80% of anh... uranyl nitrate. The solution saturated at this temperature h... approximately the composition, $UO_2(NO_3)_2,18H_2O$, and has n 1·4... and D_{15}^{15} 1·7536. T. H. P.

Alloys of Tin and Antimony. N. S. KONSTANTINOFF ... WLADIMIR A. SMIRNOFF (*J. Russ. Phys. Chem. Soc.*, 1911, 4... 1201—1220).—Investigations by the thermal method and by ... of the electrical conductivity and its temperature-coefficient ... that, after equilibrium is reached, the system Sn–Sb consists ... (1) solid solution of tin and antimony, the limiting concentrat... being 10 atom. % Sb; (2) the definite compound, SnSb, capable of dissolving up to 56% Sb; (3) the definite compound, Sn_2Sb_2, capable of dissolving up to 41% Sb; and (4) solid solution of antimony in tin, with a limiting concentration of 10 atom. % Sn. T. H. P.

Titanium. IV. ARTHUR STÄHLER and FRITZ BACHRAN (*Ber.*, 1911, 44, 2906—2915).—An improved apparatus is described for the preparation of titanium trichloride, the glass cooler and quartz ... of the previous apparatus (Abstr., 1909, ii, 894) being replaced respectively by a copper cooler and a silundum tube; the latter heated directly by passage of the electric current.

When titanium trichloride is heated at 660—700° in an atmosphere of hydrogen, the following reaction takes place: $2TiCl_3 = TiCl_2 + TiCl_4$. The tetrachloride is volatile, the dichloride remaining as a deep black powder; it was not quite pure, being contaminated with some metallic titanium. It begins to sublime at 300° in a vacuum.

The only satisfactory test for bivalent titanium is the formation of a violet colour (due to $TiCl_3$) when mixed with an hydrochloric acid solution of titanium tetrachloride.

Titanium can be obtained by heating titanium dichloride at 1100° in a current of hydrogen, the reaction being $2TiCl_2 = TiCl_4 + Ti$. A dark grey, spongy mass is obtained, which in the most favourable case contains 94·4% of titanium; the yield is not improved by heating the titanium dichloride in a vacuum.

The statement of Pfordten (Abstr., 1887, 14, 337) that titanium chloride and titanium thiochloride (TiSCl) can be obtained by leading dry hydrogen sulphide into anhydrous titanium tetrachloride could not be verified. Derivatives of quadrivalent titanium are formed, mainly of the composition $TiSCl_2$. At 800—850°, hydrogen sulphide and titanium tetrachloride interact with the formation of titanium disulphide. The compound $TiSCl_2$ could not be reduced to the monosulphide, TiS.

Titanium tetrachloride is reduced to the trichloride by heating with finely powdered aluminium, antimony, arsenic, or tin, in a sealed tube at 400°. Lower oxidation products of titanium could not be obtained by electrolysis of solutions of titanium tetrachloride in anhydrous hydrogen cyanide.

On mixing solutions of titanium trichloride and of sodium, potassium, or ammonium formates in the presence of air, olive green, microscopic needles of the double formates separate. They cannot be purified by recrystallisation from water, owing to hydrolysis, but must be washed successively with cold water, alcohol, and ether, air being excluded. The dry salts are relatively stable in the air. On being heated in the absence of air, some formaldehyde is produced. *Titanium ammonium formate*,

$$Ti(CHO_2)_3,3Ti(CHO_2)_2OH,2NH_4CHO_2,H_2O.$$

Titanium potassium formate, $Ti(CHO_2)_3,3Ti(CHO_2)_2OH,2KCHO_2$. A barium salt was also obtained in the impure condition. These salts are analogous to the acetates (Stähler and Wirthwein, Abstr., 1905, ii, 395); they may be used as mordants, owing to their ready hydrolysis in solution.

Titanium trichloride reacts with a gold solution in a similar way to stannous chloride, producing colloidal gold which is analogous to purple of Cassius. One part of gold in 20 million parts of water can be detected by this reaction. T. S. P.

The Melting Point and Frequency of Atomic Vibration of Germanium. WILHELM BILTZ (*Zeitsch. anorg. Chem.*, 1911, 72, 313—318).—Experiments with two specimens of metallic germanium by the method formerly employed to determine the melting point of certain sulphides (Abstr., 1908, ii, 845), show that germanium melts in an atmosphere of hydrogen at 958° ± 5°, but if saturated with oxide, at 916° ± 5°. It is not appreciably volatile in nitrogen at 1250°, but in the presence of some oxide, vapour is observed from 750° onwards. The oxide, GeO_2, is not volatile at 1025°. The lower oxide, GeO, is volatile. The reaction, $GeO_2 + Ge = 2GeO$, does not take place under the conditions examined.

The frequency of atomic vibration, calculated from the atomic volume, atomic weight, and melting point is 3·7.

Attempts to Prepare Bismuth Hydride. LUDWIG V... EMILIE ZUMBUSCH (*Arch. Pharm.*, 1911, **249**, 483—493). ... ing attempts to prepare bismuth hydride gave negative ... Hydrogen was passed over alloys of lead, tin, and bismuth ... of these three metals with cadmium, heated to their melting ... Aluminium, zinc, iron, cadmium, or lead was added to ... neutral solution of a bismuth compound. Bismuth mag... bismuth zinc alloy was placed in dilute acid. Calcium hyd... with bismuth compounds was moistened with water or aqueous ... of bismuth chloride.

Hydrogen was passed over mixtures of bismuth or bism... with platinum black, nickel asbestos, or reduced nickel. Pa... saturated with hydrogen was placed in a solution of bismuth ... or an electric current was passed through a cell containing ... sulphate in solution, and having an anode of palladium saturated ... hydrogen and a cathode of platinum or a cathode of bismuth ... of platinum.

Aluminium, activated by Wislicenus' method (Abstr., 189... was allowed to remain in bismuth mannitol solution or with a ... of bismuth and bismuth oxide, or in solutions of bismuth ... alcohol.

Hypophosphorous acid added to bismuth sulphate or to ... nitrate in solution gave only a precipitate of metallic bismuth ... presence of bismuth hindered the preparation of copper hydride ... this method. T. A. H.

Colloidal Gold. ALEXANDER GUTBIER (*Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 175—189. Compare Abstr., 1902, ii, 610).—The influence of temperature on the nature of the colloidal gold solutions obtained by reduction of gold chloride by hydrazine has been examined in great detail. When small quantities of aqueous hydrazine are added to dilute gold solutions, blue hydrosols are produced at the ordinary temperature, whereas at 80°, 90°, and 100° the colour is red, or more usually reddish-violet. The same result is obtained when the procedure is reversed by adding small quantities of the gold chloride solution to very dilute hydrazine, except that in this case violet hydrosols are occasionally formed even at the ordinary temperature. The addition of electrolytes or of gum arabic as protective colloid is without influence on the nature of the products.

The colloidal solutions prepared at 100° are very sensitive towards electrolytes. The addition of a few drops of 0·1*N*-solutions at the ordinary temperature gives rise quickly to a blue solution of colloidal gold. H. M. D.

Dichloro-disulphaminoplato-salts. The Stereoisomerism of Platinum and the Transformation of Sulphamic Acid. HEINRICH KIRMREUTHER (*Ber.*, 1911, **44**, 3115—312...). By the action of potassium platinochloride on sulphamic acid

[Two] *potassium dichlorodisulphaminoplatinites* have been obtained, the α-salt, $[Cl_2Pt(NH_2\cdot SO_3)_2]K_2,2H_2O$, being yellow and readily soluble, whilst the β-salt, $[Cl_2Pt(NH_2\cdot SO_3)_2]K_2$, is almost colourless and more difficultly soluble. Both salts contain only the potassiums in an ionogenic condition and both are neutral, so that they cannot be structural isomerides in accordance with the formulæ:

$$[Cl_2Pt(\cdot SO_3\cdot NH_2)_2]K_2$$

and $[Cl_2Pt(\cdot NH\cdot SO_3H)_2]K_2$. Both salts dissolve in potassium hydroxide, giving an intense golden yellow solution containing a tetra-potassium salt; they must, therefore, be derived from the second of the above formulæ, that is, they are platosimines. Acids re-precipitate the salts from the solution in potassium hydroxide. The author considers them to be stereoisomerides, similar to the dichloroplatosamines, and from analogy to already known isomerides of platinum, the α-salt is characterised as the cis-form, $\left[\begin{matrix}Cl\\Cl\end{matrix}>Pt<\begin{matrix}SO_3\cdot NH_2\\SO_3\cdot NH_2\end{matrix}\right]K_2$, and the β-salt as the *trans*-form, $\left[\begin{matrix}Cl\\NH_2\cdot SO_3\end{matrix}>Pt<\begin{matrix}SO_3\cdot NH_2\\Cl\end{matrix}\right]K_2$.

Potassium cis-*dichlorodisulphaminoplatinite* is obtained by the interaction of potassium platinochloride (1 mol.) and sulphamic acid (2 mols.) in cold aqueous solution. After keeping for twenty-four hours the solution deposits tabular, golden yellow crystals, which are weakly pleochroitic; they belong probably to the rhombic system, and are soluble to the extent of 1 part in 38 parts of water at 21°. $1H_2O$ is lost at 90° and $2H_2O$ at 130°. Barium chloride and hydrochloric acid give no precipitate, even on warming, proving that the sulphamic acid residue is in the inner complex sphere. Pyridine replaces the sulphamic acid from the residue, giving *cis*-dichloro-dipyridine-platinum.

Potassium trans-*dichlorodisulphaminoplatinite* is obtained when more than 2 mols. of sulphamic acid react with 1 mol. of potassium platinochloride, the reaction being best carried out on the water-bath. After heating for two to three hours, the solution, on cooling, deposits a mass of almost colourless, felted needles, which dissolve in water to the extent of 1 part in 342 parts at 21°. The reactions of this salt are similar to those of the *cis*-isomeride, except that pyridine gives *trans*-dichloro-dipyridine-platinum.

Tetrapotassium trans-*dichlorodisulphiminoplatinite*,

$$[Cl_2Pt(NH\cdot SO_3)_2]K_4,$$

is obtained by dissolving the above salt in potassium hydroxide and precipitating the solution with alcohol. It forms intense yellow, radiating clusters of prisms, and gives a strongly alkaline solution.

Potassium trans-*dibromodisulphaminoplatinite*,

$$[Br_2Pt(SO_3NH_2)_2]K_2,$$

and *potassium* trans-*di-iodo-disulphaminoplatinite*,

$$[I_2Pt(SO_3NH_2)_2]K_2,$$

were obtained from the dichloro-compound by interaction with potassium bromide and iodide respectively. The former gives bright orange-yellow prisms, whilst the latter forms reddish-brown prisms.

T. S. P.

Mineralogical Chemistry.

Atacamite. HENRI UNGEMACH (*Bull. Soc. franç. Min.* [illegible] 148—216).—A monograph of the species. In the new [illegible] the crystals (the axes *b* and *c* being interchanged) [illegible] are $a:b:c=0.87808:1:1.32710$. Many new crystal-forms [illegible] Crystals from Antofagasta, Chili, have D 3·769, 3·778, [illegible] Boleo, Lower California, Mexico, 3·774, 3·776. Previous analyses [illegible] tabulated, and the following new ones are given. The [illegible] form assigned to paratacamite (G. F. H. Smith, Abstr., [illegible] is explained by twinning on $e(011)$ of atacamite according [illegible] law of W. E. Ford (*Amer. J. Sci.*, 1910, **30**, 16).

	Cl.	Cu.	CuO.	[illegible]
Antofagasta	16·48	14·75	55·81	[illegible]
Boleo	16·22	14·53	55·33	[illegible]

L. J. S.

Schwartzembergite. G. F. HERBERT SMITH and GEORGE [illegible] (*Min. Mag.*, 1911, **16**, 77—83).—Crystals of schwartzembergite [illegible] San Rafael mine, Sierra Gorda, Chili, are tetragonal (not rhombic [illegible] as previously stated) with $a:c=1:0.430$, and have the form [illegible] square pyramids with rounded faces. They are optically [illegible] showing a division into sectors with optic axial angles 2V [illegible] and 28°; refractive index about 2·35. The colour is honey-yellow [illegible] brownish or reddish, and the powder is straw-yellow. Analysis [illegible]

Pb.	Cu.	CaO.	Cl.	I.	SO_3.	O and loss.	Sp. [illegible]
75·07	trace	0·67	7·96	8·64	0·47	[7·19]	7 [illegible]

The calcium sulphate is present as gypsum. Calculating [illegible] results as an oxychloroiodide of lead (as done for previous analyses) there is still a deficit of nearly 4%. When the mineral is heated [illegible] hydrochloric acid, abundant chlorine is evolved, and in the cold [illegible] acid solution the iodine is present as iodate, and not as iodide. [illegible] formula is, therefore, written as $3(PbCl_2,2PbO),PbI_2O_6$, representing a molecular compound of lead iodate with a lead oxychloride [illegible] the composition of mendipite. L. J. S.

Micro-structure of Magnetite. OTTO MÜGGE (*Jahrb. Min. Beil.-Bd.*, 1911, **32**, 491—534).—Etching experiments were made on crystals and plates of magnetite and of some other minerals of the [illegible] group, and a detailed description illustrated by many photomicrographs is given of the resulting etched surfaces. When a crystal of magnetite is placed in freshly fused potassium hydrogen sulphate it is only very slightly attacked, but at a higher temperature, when the free sulphuric acid has been largely expelled, there is an energetic action. An octahedral face of an etched crystal shows a shimmer in three positions. This is shown to be due to a regular orientation of minute crystals of hæmatite on the magnetite, the basal plane of the former being parallel to the octahedral face of the latter. A similar result is

obtained when magnetite crystals are heated in the air; and the martite pseudomorphs are shown to possess a similar structure. Hæmatite when heated in nitrogen at about 1500°, or in the presence of a reducing agent at the lower temperature of 700°, loses part of its oxygen, and magnetite is developed on its surface in regular orientation. L. J. S.

A Ferriferous Dolomite from the Simplon Tunnel. GABRIELLE LINCIO (*Atti R. Accad. Sci. Torino*, 1911, 46, 969—988).—The mineral was found about 4590 metres from the Italian end of the tunnel, and was deposited in association with calcite and other minerals. It has D 3·003 at 14—15°, and on analysis gave the following numbers:

CaO.	MgO.	FeO.	CO_2.	Total.
29·61	12·94	12·99	44·72	100·26

corresponding with the formula: $3CaCO_3,2MgCO_3,FeCO_3$. The mineral is crystalline, and contains included many minute gaseous bubbles. R. V. S.

The Distribution of Borates in Potash Deposits. WILHELM BILTZ and E. MARCUS (*Zeitsch. anorg. Chem.*, 1911, 72, 302—312).—The distribution of borates has been studied in the same specimens from the Stassfurt and Vienenburg deposits as have been already used for the estimation of nitrogen and of copper (Abstr., 1909, ii, 571, 1011) together with specimens from other German deposits. Special samples have also been analysed, taken from the immediate neighbourhood of the concretions of boracite, and at definite distances from them. The proportions found vary from 0·4% in some of the salt clays to 0·01% in carnallite and kieserite, whilst the polyhalite region is free from borates. Most of the boric acid is found in the residue insoluble in water. Where lenses of rock salt are enclosed in carnallite, the veins contained in these lenses are much richer in borates than those of the typical older salts. No such regularity is found in the distribution of borates as in that of ammonia and bromine. The proportion of borates is slightly lowered in the immediate neighbourhood of boracite concretions.

The turmeric test is sensitive to 0·00005 milligram B_2O_3 in 1 c.c. The quantitative estimation is best performed by Wherry's method (Abstr., 1909, ii, 92). C. H. D.

The Alunite-Beudantite Group. WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], 32, 359—364).—The minerals of this group (compare G. T. Prior, Abstr., 1903, ii, 377) are all rhombohedral, but they often exhibit optical anomalies. They fall into the following three sub-groups of sulphates, phosphates, and sulphato-phosphates, of which alunite, hamlinite, and beudantite respectively may be taken as the types. The general formula is written $[R'''(OH)_2]_3R''[M]_2[M_2]$.

Various incompletely-described minerals, which may possibly belong to this group, are discussed. It is suggested that goyazite is identical with hamlinite; and utahite, carphosiderite and its aluminous variety

apatelite, raimondite, pastreite, and cyprusite are all united ... name carphosiderite, with the new formula $3Fe_2O_3,4SO_3,7H_2O$ ...

Sulphates	Alunite	$[Al(OH)_2]_6$	K_2	$[SO_4]_2$	[SO...
	Natroalunite	$[Al(OH)_2]_6$	Na_2	$[SO_4]_2$	[SO...
	Jarosite	$[Fe(OH)_2]_6$	K_2	$[SO_4]_2$	[SO...
	Natrojarosite ...	$[Fe(OH)_2]_6$	Na_2	$[SO_4]_2$	[SO...
	Plumbojarosite ...	$[Fe(OH)_2]_6$	Pb	$[SO_4]_2$	[SO...
	Carphosiderite ...	$[Fe(OH)_2]_6$	H_2	$[SO_4]_2$	[SO...
Phosphates	Hamlinite ...	$[Al(OH)_2]_6$	Sr	$[HPO_4]_2$	[Sr...
	Plumbogummite ...	$[Al(OH)_2]_6$	Pb	$[HPO_4]_2$	[P...
	Gorceixite ...	$[Al(OH)_2]_6$	Ba	$[HPO_4]_2$	[B...
	Florencite ...	$[Al(OH)_2]_6$	Ce_1	$[Ce_1PO_4]_2$	[Ce...
Sulphate-phosphates	Beudantite	$[Fe(OH)_2]_6$	Pb	$[SO_4]_2$	[P...
	Corkite ...	$[Fe(OH)_2]_6$	Pb	$[SO_4]_2$	[P...
	Svanbergite ...	$[Al(OH)_2]_6$	Sr	$[SO_4]_2$	[Sr...
	Hinsdalite ...	$[Al(OH)_2]_6$	Pb	$[SO_4]_2$	[P...
	Harttite	$[Al(OH)_2]_6$	Sr	$[SO_4]_2$	[SO...
		$2[Al(OH)_2]_6$	Sr	$[HPO_4]_2$	[Sr...

with that in the above table). The formula of pharmacosiderite ... written in the form $2(H,K)_2O,3Fe_2O_3,2As_2O_5,7H_2O+4H_2O$ ... that this mineral may also belong to the hamlinite sub-group.

L. J. S.

Composition of French Phosphorite Minerals. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1911, 1, 151). Lacroix ... regarded the French phosphorites as mixtures of collophanite, dahllite (= podolite), and francolite (= staffelite), and he has ascribed cert... formulæ to those species (Abstr., 1910, ii, 622, 720). A study of ... published analyses leads to the following formulæ as more probable:

Dahllite	$9CaO,3P_2O_5,CaO,CO_2,H_2O$
Francolite	$9CaO,3P_2O_5,CaF_2,CO_2,H_2O$
Collophanite ...	$9CaO,3P_2O_5,CaO,CO_2,H_2O+nH_2O$

L. J. S.

Herderite Crystals from Auburn, Maine. WILLIAM F. F... (*Amer. J. Sci.*, 1911, [iv], 32, 283—286).—A crystallographic description is given of herderite crystals from Mt. Apatite, Au... Maine, which are of interest, in that some of them are untwinned ... distinctly monoclinic, whilst others show the union of two individuals twinned on the basal plane, so producing the pseudo-orthorhombic forms characteristic of this mineral. The measured angles approach more closely those of Penfield (1894) for the hydro-herderite, $Ca[Gl(OH)]PO_4$, from Paris, Maine, than those of Dana (1884) for the hydro-fluor-herderite, $Ca[Gl(F,OH)]PO_4$, from Stoneham, Maine. A partial analysis of the crystals gave, however, F = 6·04%, H_2O = 3·62%, proving the material to be hydro-fluor-herderite. The suggestion of Penfield that the angles of the crystals vary with the composition is therefore not supported. Penfield's angles are adopted for both varieties as being the most trustworthy. L. J. S.

Hinsdalite, a New Mineral. ESPER S. LARSEN, jun., and WALDEMAR T. SCHALLER (*Amer. J. Sci.*, 1911, [iv], 32, 251—255).—This new mineral occurs in considerable abundance at the Golden

[illegible] Mine, near Lake City, Hinsdale Co., Colorado, where, together with quartz, it forms the gangue of a vein intersecting volcanic rocks. Associated minerals in the vein are barytes, iron-pyrites, galena, tetrahedrite, and rhodochrosite. The hinsdalite is granular and coarsely crystalline, with a dark grey colour and a vitreous to greasy lustre. Crystals are nearly colourless with a greenish cast; they have the form of cube-like rhombohedra (rr = 91 18′) or of six-sided plates. There is a perfect cleavage parallel to the base; H. = 4½; sp. gr. 3·65. The crystals are zoned and exhibit optical anomalies; an optically uniaxial centre is surrounded by sectors with axial angles (E [illegible]). Refractive indices, α = 1·670, β = 1·671, γ = 1·689. Analysis gave:

PbO.	SrO.	CaO.	Al_2O_3.	SO_3.	P_2O_5.	H_2O.	Total.
[illegible]	3·11	trace	26·47	14·13	14·[illegible]	[illegible]	100·21

corresponding with $2PbO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$, mixed with 17·44% of the svanbergite molecule. The mineral is infusible and is practically insoluble in acids; its water is lost between 400° and 600°. Hinsdalite therefore falls into the following isomorphous group:

		Rhombohedral $a : c$.
Svanbergite	$2SrO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$	1 : 1·2063
Hinsdalite	$2PbO,3Al_2O_3,2SO_3,P_2O_5,6H_2O$	1 : 1·9677
Corkite	$2PbO,3Fe_2O_3,2SO_3,P_2O_5,6H_2O$	1 : 1·1842
Beudantite	$2PbO,3Fe_2O_3,2SO_3,As_2O_5,6H_2O$	1 : 1·1842

L. J. S.

Crystallised Variscite from Utah. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1911, **1**, 150—151).—The bright green crystals from Lucin, Utah, are orthorhombic with a tabular habit or a form similar to those of the analogous minerals, scorodite and strengite (phosphosiderite). They are only slightly pleochroic, and have a mean refractive index of 1·560 and birefringence 0·032. All the water is lost at 160°, and the crystals become lavender-coloured with strong pleochroism, mean refractive index 1·448, and birefringence 0·063. The dehydrated material is readily soluble in acids, whilst the green crystals are sparingly soluble. Analysis agrees with the usual formula $Al_2O_3,P_2O_5,4H_2O$:

P_2O_5.	V_2O_5.	Cr_2O_3.	Fe_2O_3.	Al_2O_3.	H_2O.	Total.	Sp. gr.
44·73	0·32	0·18	0·06	32·[illegible]	22·[illegible]	100·37	2·54

L. J. S.

Fermorite and Tilasite from the Manganese-ore Deposits of India. G. F. HERBERT SMITH and GEORGE T. PRIOR (*Min. Mag.*, 1911, **16**, 84—96).—The new mineral fermorite forms veins of pale pinkish-white or white material in the manganese ore (a mixture of braunite, hollandite, and pyrolusite) at Sitapar, Central Provinces. It is translucent with a greasy lustre, and is optically uniaxial and negative. One specimen showed a prism of 60°, proving the mineral to be hexagonal, and, as seen from analysis I, isomorphous with apatite. Formula: $3[(Ca,Sr)_3(P,As)_2O_8],Ca(OH,F)_2$.

	As_2O_5.	P_2O_5.	FeO.	CaO.	SrO.	MgO.	F.	H_2O.	Insol.	Total less O for F.	Sp. gr.
I	25·[illegible]	20·11	—	44·34	9·93	—	0·[illegible]	trace	0·08	100·17	3·518
II	[illegible]·35	0·43	0·55	25·68	0·66	18·[illegible]	7·18	0·73	0·05	100·35	3·77

Tilasite occurs as pale green, translucent to opaque cry... what resembling apatite in appearance, in a quartz ... traversing the manganese-ore, and in a quartz-spessart... rock; both occurrences are at Kajlidongri, Jhabua ... crystals are monoclinic [$a:b:c = 0.7503:1:0.8391$; β ... are of interest in belonging to the clinohedral class, ... plane of symmetry, but no axis of symmetry. The optic ... is perpendicular to the plane of symmetry; $2V = 82°44'$ ... $\beta = 1.660$, $\gamma = 1.675$(Na). Analysis II gives the ... $(MgF)CaAsO_4$. The identity of the mineral with ... fluor-adelite from Sweden (Sjögren, 1895) is discussed. ...

Analyses of Stibiotantalite. WILLIAM E. FORD (*Amer. J. Sci.*, 1911, [iv], 32, 287—288).—In the analyses of stibiotantalite ... San Diego Co., California (Penfield and Ford, Abstr., 190..., ii, ...) the relative amounts of tantalum and columbium were ... indirectly from the specific gravity of the mixed oxides ... assumption that the composition and sp. gr. vary propor... It has been shown, however, by Foote and Langley (Abstr., ..., ii, 71) that the curve obtained by plotting the sp. gr. against ... composition is not quite a straight line; the oxides apparent... a solid solution, and do not exist together simply as a mec... mixture. From the table of Foote and Langley a correction of ... 2% is to be made in the old analyses, which are re-calculated ... I and II. Under III are given the results of a new analy... Foote and Langley:

	Ta_2O_5.	Cb_2O_5.	Sb_2O_3.	Bi_2O_3.	Total.	Sp. gr.
I.	13·00	37·30	49·28	0·53	100·11	[illegible]
II.	33·86	21·47	44·26	0·33	99·92	[illegible]
III.	41·92	16·19	40·95	0·60	99·66	[illegible]

L. J. S.

Trans-Baikal Minerals. S. D. KUSNETZOFF (*Bull. Acad. Sci. St. Pétersbourg*, 1911, 897—901).—Descriptions are given of the following minerals.

Powellite, in crusts of white plates. Composition:

MoO_3.	CaO.	Fe_2O_3,Al_2O_3.	SiO_2.	Total.
70·05	25·10	3·45	1·80	100·50

The original powellite from Idaho contained 10·28% WO_3.

Bismuthospherite.—Two specimens: (a) greenish-brown, D 7·00, and (β) apple-green, D 6·86, gave on analysis, after allowing for insoluble residue:

Bi_2O_3.	CO_2.	H_2O.	Total.
90·13—90·19	9·23—9·11	0·64—0·70	100

Pure bismuthospherite, Bi_2CO_5, contains Bi_2O_3 91·3, and CO_2 8·7.

T. H. P.

A New Variety of Chrysocolla from Chile. HARRY F. KELLER (*Proc. Amer. Phil. Soc.*, 1909, 48, 65—66).—Chrysocolla shows wide

[illegible] in composition, and the colour ranges from bright green to [illegible] Analyses of green material agree with the formula

$CuSiO_3,2H_2O$.

[illegible] wing analyses are given of turquoise-blue material occurring [illegible] like crusts in a honey-combed, siliceous matrix from [illegible], prov. Tarapaca, Chile. It is brittle, H. [illegible]; and is [illegible] decomposed by acids without gelatinisation. The powder is [illegible] green. It blackens when heated; two-thirds (13·41%) of the [illegible] lost below 125°, and the remainder only at a red heat. The [illegible] is therefore written as a hydrated acid [illegible],

$CuH_2(SiO_3)_2,H_2O$:

	CuO.	Al_2O_3.	FeO.	CaO.	MgO.	H_2O.	Total.	Sp. gr.
[illegible]	28·85	0·58	1·[illegible]	1·64	[illegible]	[illegible]	[illegible]	2·532
[illegible]	28·69	0·47	1·[illegible]	1·67	[illegible]	[illegible]	[illegible]	[illegible]

L. J. S.

Beryl and Rhodizite from the Pegmatites of Madagascar. [illegible] DUPARC, M. WUNDER, and R. SABOT (*Bull. Soc. franç. Min.*, [illegible], 34, 131—139).—A crystal of beryl from Maharitra, of tabular [illegible] and rich in faces, differs from those previously described from [illegible] locality (Abstr., 1910, ii, 312; 1911, ii, 736) in being much [illegible] and in its pale bluish-green (instead of rose-red) colour. [illegible] 2·8474; refractive indices (Na light), ω 1·5974, ε 1·5890. Analysis I.—These results confirm the presence in the Madagascar pegmatites of two types of beryl: one the ordinary aquamarine with prismatic habit and few crystal-faces, low density and refractive indices, poor in alkalis, and without cæsium and rubidium; the other [illegible] tabular habit parallel to the base and rich in faces, with higher density and refractive indices, and rich in alkalis, particularly cæsium and rubidium:

	SiO_2.	Al_2O_3.	GlO.	MgO.	K_2O.	Na_2O.	Li_2O.	Cs_2O.	Rb_2O.	Loss on ignition.	Total.
I.	[illegible]	17·41	11·76	trace	0·68	2·05	1·[illegible]	[illegible]	[illegible]	2·[illegible]	99·97
II.	[illegible]	27·40	14·93	0·11	1·41	1·78	0·68	[illegible]·47	2·[illegible]	1·42	*

* B_2O_3, by difference, 13·[illegible].

Rhodizite occurs in association with rubellite at Ampakite in the Sahatany valley. The two crystals described have the form of the rhombic dodecahedron with small tetrahedral faces; they are, however, pseudo-cubic and birefringent; refractive index (Na) 1·6935 (and [illegible]); D 3·344. The crystals are translucent with a vitreous lustre, [illegible] yellow with a tinge of green. Analysis II, corresponding with $B_{[illegible]}Al_{[illegible]}Gl_{[illegible]}(Li,K,Cs,Rb,Na,H)_4O_{[illegible]}$, differs appreciably from Pisani's analysis (Abstr., 1910, ii, 57) of rhodizite from Madagascar.

L. J. S.

Samarskite, etc., from Madras. GEORGE HOWLETT TIPPER (*Rec. Geol. Surv. India*, 1911, 41, 210—213). Angular masses of samarskite, up to 200 lb. in weight, occur in a garnet-bearing pegmatite in the Sankara mica mine in Nellore district, Madras. On the conchoidal fracture it is black with a brilliant lustre; D 5·4—5·7. It is a columbate and tantalate of cerium and yttrium earths, with iron,

calcium, and very variable amounts of uranium. Associated with it are long, black crystals resembling allanite, but differing from that in containing 17·8% Cb_2O_5 and 5·39% U_3O_8; it contains also the cerium earths; D 3·05. Another associated mineral is a hydrated zircon resembling cyrtolite, but containing some uranium. This occurs as sheaf-like groups of pale greyish-brown crystals, D 4·69. The following analysis corresponds with the formula $2ZrSiO_4,H_2O$. The powdered mineral is attacked by hot concentrated hydrochloric acid, and, after one hour, 15% is dissolved, all the iron and part of the zirconia going into solution:

ZrO_2.	SiO_2.	Fe_2O_3.	Ce_2O_3, etc.	MnO.	U_3O_8.	H_2O.	Total.
62·3	26·06	5·41	trace	trace	2·42	3·3	99·49

L. J. S.

Meteoric Iron from Currant Creek, Colorado. William P. Headden (*Proc. Colorado Sci. Soc.*, 1908, 9, 79—80).—This mass of 596 lbs. was found about 1906 at Currant Creek, twenty-two miles south-west of Cripple Creek. It shows no Widmanstätten figures on a polished and etched surface. Analysis gave:

Fe.	Ni.	Co.	Mn.	Cr.	Cu, P, CaO, MgO.	S, [illegible]
89·793	9·999	0·554	0·054	0·048	traces	[illegible]

L. J. S.

Chemical and Petrological Examination of the El Nakhla Meteorite. Stanislas Meunier (*Compt. rend.*, 1911, 153, 785—787).—This meteorite, which fell recently near Alexandria, shows a remarkably crystalline structure, and consists principally of fragments of hypersthene (83·34%) united by a cement soluble in hydrochloric acid. The hypersthene shows the macled structure, and contains inclusions of ilmenite. Analysis gave:

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O and Na_2O.	MnO.	Total.
47·40	0·69	20·80	15·20	14·61	0·05	0·85	99·60

W. O. W.

The Gas of the Boriferous "Soffioni" of Larderello. C. Porlezza and G. Norzi (*Atti R. Accad. Lincei*, 1911, [v], 20, ii, 338—342).—A new analysis of the gas from this source has given results very similar to those of Nasini, Anderlini, and Salvadori (Abstr., 1898, ii, 527). The principal differences occur in the case of the rare gases, for which more accurate methods are now available. The gas has the following composition:

CO_2.	H_2S.	CH_4.	H_2.	O_2.	N_2.	A.	He.	Total.
92·2000	2·0000	1·7800	2·4500	0·1800	1·3500	0·0245	0·0155	100·0000

The quantity of radium emanation in the gas amounts to $4·813 \times 10^{-7}$ c.mm.

R. V. S.

Physiological Chemistry.

The Nitrous Oxide Method of Estimating the Quantity of Blood in the Body. I. MARKOFF, FRANZ MÜLLER, and NATHAN ZUNTZ (*Zeitsch. Balneol., Klimatol. Kurort-Hygiene*, 1911, 4, Nos. 14, 15. Reprint, 16 pp.).—By allowing a person or animal to breathe a measured quantity of nitrous oxide and subsequently examining a sample of the blood, and estimating the tension of the gas in it, the total volume of the blood can be calculated. The difficulty of estimating the gas can be largely overcome by the use of the gas interferometer. The influence of bath-treatment, climate, work, etc., on the blood volume is to be investigated by this method.

W. D. H.

Action of Extracts of Invertebrate Tissues on Blood-pressure. JEAN GAUTRELET (*Bull. stat. biol. d'Arcachon*, 1910, 13, 53—63).—The hepato-pancreas of the crab, and of *Maia*, contains one or more substances slightly soluble in alcohol which lower the blood-pressure of the dog when intravenously injected. Aqueous or alcoholic extracts of the genital glands are inactive. Among molluscs, extracts of the genital glands and of the liver in *Sepia*, *Octopus*, and *Aplysia* (liver only) depress blood-pressure and diminish cardiac action. The same is true for echinoderms. In cases where depression of blood-pressure occurs, previous administration of atropine does not influence the result.

W. D. H.

The Size, and the Growth of the Blood in Tame Rats. R. A. CHISOLM (*Quart. J. exp. Physiol.*, 1911, 4, 207—230).—The average oxygen capacity per kilo. of rats weighing from 50 to 150 grams each is 10 c.c., and the blood volume 63 c.c. The average hæmoglobin percentage is 86, and the number of red corpuscles 9 million per cubic millimetre. A fall in hæmoglobin, oxygen capacity, and blood volume occurs temporarily during the suckling period, and a fall in blood volume takes place in later life as the rate of growth diminishes. The oxygen capacity is less variable than the other factors mentioned. The volume of the blood in rats may be calculated by the formula $a^{0.9}/10.1$, and the total oxygen capacity by the formula $a^{0.95}/8$, where a is the body-weight.

The volume of the blood is less variable than the weight of kidneys, liver, and spleen considered as percentages of the body-weight.

W. D. H.

The Influence of Under-feeding on the Blood. ARTHUR E. BOYCOTT and R. A. CHISOLM (*J. Path. Bact.*, 1911. 16, 263—268).—Under-feeding with a diet deficient in protein does not necessarily cause any wasting of the blood in rats. It is suggested that this result throws some light on the duration of life of the red corpuscles.

W. D. H.

The Influence on the Blood of the Rat of the Presence of a Transplanted Sarcoma. R. A. Chisolm (*J. Path. Bact.*, 1911, 16, 152—166).—Transplanted sarcomata in rats usually produce a diminution in oxygen capacity and in hæmoglobin percentage, which is parallel to the decrease in red corpuscles. The volume of the blood is increased. The anæmia is usually accompanied by wasting of the tissues. The blood histologically shows signs of regeneration, but the mechanism of the blood destruction is unknown. In small tumours occasionally the oxygen capacity and the blood volume increase to meet the needs of the tumour. W. D. H.

The Fat-splitting Properties of the Blood and Serum of the Dog under Different Conditions. Emil Abderhalden and Peter Rona (*Zeitsch. physiol. Chem.*, 1911, 75, 30—37).—The introduction of foreign blood into the circulation raises the fat-splitting power of the dog's blood, and especially of the serum. W. D. H.

The Individual Differences of the Red Blood-corpuscles on Hæmolysis. Stephan Rusznyák (*Biochem. Zeitsch.*, 1911, 36, 394—396).—The author denies the correctness of the conclusions of Dienes (this vol., ii, 740), that the corpuscles show individual differences on hæmolysis, on the ground that Dienes has assumed that the dried matter of the blood-corpuscles contains 50% hæmoglobin, whereas Abderhalden has shown that they contain 77%. If Dienes' results are calculated on the latter assumption, his conclusions cannot be substantiated. S. B. S.

The Action of Selenium Salts on Red Blood-corpuscles. Charles O. Jones (*Bio.-Chem. J.*, 1911, 6, 106—109).—Sodium selenite does not produce hæmolysis outside the body, but does so after hypodermic injection. The cause of this is obscure. Sodium selenite is reduced to selenium in the portal circulation, chiefly in the spleen and liver. Only a proportion of the red corpuscles are hæmolysed, suggesting that these from the portal system were mixed in the general circulation with those which are unaffected. Glycogen and sugar disappear in a remarkable manner after the injection, but whether this is a factor in hæmolysis is very questionable. W. D. H.

The Rate of Regeneration of Hæmoglobin after Hæmorrhage. Arthur E. Boycott (*J. Path. Bact.*, 1911, 16, 269—275).—Rats regenerate hæmoglobin after hæmorrhage more quickly than do rabbits, roughly in the proportion of three or four to one. Young rats and rabbits regenerate more quickly than adults. W. D. H.

The Enzymes of Leucocytes. M. Tschernoruzki (*Zeitsch. physiol. Chem.*, 1911, 75, 216—231).—The polynuclear leucocytes of the dog carry the following enzymes: protease, amylase, diastase, catalase, nuclease, and peroxydase, but not lipase. W. D. H.

Biotoxin. Francesco Marino-Zuco, R. Onorato, and L. Giuganino (*Gazzetta*, 1911, 41, ii, 358—367. Compare Abstr., 1910, ii, 223, and this vol., i, 1049).—When its excretion by way of the kidneys is interfered with, biotoxin accumulates in the blood, but its quantity does not increase

indefinitely, so that a part of the toxin must be eliminated in some way. The suppression of the renal secretion was effected in dogs in three ways; (1) by extirpation of the kidneys; (2) by cutting the ureters; (3) by producing an artificial nephritis. R. V. S.

The Acidity of the Gastric Juice of Scyllium Stellare. (Fraulein) H. A. VAN HERWERDEN and WILHELM E. RINGER (*Zeitsch. physiol. Chem.*, 1911, **75**, 290—307).—Fraulein van Herwerden in her first paper showed that the Sjoqvist method was inapplicable to the investigation of the gastric juice of the dog-fish; the acidity is quite considerable, and she believed it might possibly be due to organic acid. A method was devised for testing this question with artificial juice, and found trustworthy. Applying it to the dog-fish juice, the conclusion is now reached that the major part of the acidity is due to hydrochloric acid; this was confirmed by actual analyses.

W. D. H.

Digestion of Casein. LOUIS GAUCHER (*Compt. rend.*, 1911, **153**, 891—892. Compare Abstr., 1909, ii, 249, 236).—The experiments on dogs described in the earlier communications have been repeated on a boy, in whom, owing to the necessity of an operation, a fistula had been established at the opening of the jejunum. The curdling of milk in the stomach is not necessary to digestion, since a considerable amount passes into the intestine without having coagulated. The larger clots are broken up into much smaller fragments by the movements of the stomach; if the organ is incapable of effecting this, digestion may be hindered. No peptonisation occurs until the milk has passed the duodenum. W. O. W.

Studies in Nutrition. I. The Utilisation of the Proteins of Wheat. LAFAYETTE B. MENDEL and MORRIS S. FINE (*J. Biol. Chem.*, 1911, **10**, 303—325).—It has been held in the past that vegetable proteins are not utilised as thoroughly in the body as those of animal origin. The indigestibility of such proteins is largely due to unfavourable concomitant conditions, of which the most important is admixture with cellulose. In the present experiments such conditions were eliminated as far as possible, and it was found in men and dogs that glidin (a commercial product, which is mainly gliadin, and is free from starch), gluten (also commercial), and the two characteristic proteins of wheat, gliadin and glutenin, are as thoroughly utilised as are the nitrogenous components of fresh meat. W. D. H.

Studies in Nutrition. II. The Utilisation of the Proteins of Barley. LAFAYETTE B. MENDEL and MORRIS S. FINE (*J. Biol. Chem.*, 1911, **10**, 339—343).—Under favourable conditions, barley protein, like that of the closely related cereal, wheat, would be almost perfectly digested. W. D. H.

The Resorption of Gelatin from the Small Intestine. FELIX REACH (*Biochem. Zeitsch.*, 1911, **36**, 498).—The author recalls his own experiments (Abstr., 1901, ii, 667), in which the time of action was

five and a-half hours, whereas in Minami's experiments (this vol., ii, **810) the time of action was only one hour.** S. B. S.

Physiology of Digestion. IV. The Total Chlorine of the Animal Body on a Diet Rich in Chlorine. Rudolf Rosemann (*Pflüger's Archiv*, 1911, **142**, 447—458. Compare Abstr., 1911, ii, 1082).—The percentage of chlorine in the body of the normal dog is 0·112. On food poor in chlorine this falls. The present research deals with the effect of a diet rich in chlorine, and consists of experiments on two dogs. In the first, the feeding was continued for three weeks. The chlorine rose to 0·136%, but that of the skin was [illegible] greater than that of the body as a whole. In the second, the feeding was kept up for two months. The percentage in the whole body rose to 0·163%, and of the skin to 0·342%, which confirms the statements previously made concerning the skin as a chlorine depot. The percentage in the blood was also high (0·308%). W. D. H.

Physiology of Digestion. V. The Total Chlorine of the Human Fœtus. Rudolf Rosemann (*Pflüger's Archiv*, 1911, **142**, 459—460).—That the fœtus has a high percentage of chlorine is confirmed by the analyses recorded of a human fœtus 18 centimetres long; it contained 0·252% of chlorine. W. D. H.

Chemistry of the Hen's Egg. Kenji Kojo (*Zeitsch. physiol. Chem.*, 1911, **75**, 1—12).—The following analytical figures are given:

	White.	Yolk.
Water	87·71	49·73
Total solids	12·29	50·27
Ash	0·4	1·44
Organic solids	11·89	48·83
Total nitrogen	1·75	2·49
Dextrose	0·55	0·27

W. D. H.

Biology of the Egg, a Chemico-Anatomical Co-ordination. Vincenzo Diamare (*Anat. Anzeiger*, 1911, **40**, 205—207).—The eggs of birds and reptiles contain dextrose, which is apparently formed from the living material present. The bulk of the paper is polemical against Salkowski, who, it is complained, has misrepresented the author's views on the part played by sugar in development.

W. D. H.

The Catalase of Sea-Urchin Eggs Before and After Fertilisation, with Especial Reference to the Relation of Catalase to Oxidation in General. Samuel Amberg and M. C. Winternitz (*J. Biol. Chem.*, 1911, **10**, 295—302).—The fertilisation of sea-urchin's eggs leads to an increase of four to six times its cell oxidation, but this is not accompanied by an increase in its catalytic activity.

W. D. H.

Are the Oxidative Processes Independent Variables in Vital Processes? Jacques Loeb and Hardolph Wasteneys (*Biochem. Zeitsch.*, 1911, **36**, 345—356).—The experiments were

carried out with the eggs of sea-urchin (*Arbacia*), and the temperature-coefficients of oxidation and rate of development were determined. The latter was estimated by determining the time elapsing between fertilisation with the spermatozoa and the first bifurcation of the eggs. The temperature-coefficients for both processes between 15° and 30° were found to be nearly identical (= about 2). The temperature-coefficient for the development rate increased with decreasing temperature, whereas that of the oxidation process remained nearly constant. The amount of sodium cyanide necessary to just inhibit development did not decrease the oxidative process by quite one-quarter of the total. This fact is in harmony with the discovery that the rate of oxidative processes is increased by about one-quarter by fertilisation. From these facts it can be understood why the temperature-coefficients of oxidation and development rate are no longer identical at lower temperatures. At temperatures above 32°, at which bifurcation is impossible, the oxidative processes also rapidly diminish. The results, without confirming the hypothesis that the oxidative processes are independent variables in the development of the egg, do not contradict it. S. B. S.

Chemical and Physiological Examination of the Liver of Oxen. A. DANIEL-BRUNET and C. ROLLAND (*Compt. rend.*, 1911, 153, 900—902).—The bile of oxen gave the following analytical results, stated to be more complete than any hitherto published. The weights are in grams per kilogram of fresh material. The amount of bile from one animal varied from 335 to 630 c.c. It had $D^{?}$ 1·024—1·027, and gave an extract, dried in a vacuum, of 80·3—90·5; dried at 100°, 88·5—92·5; at 110°, 86·80 to 89·60. Ash, 12·5—14·30; chlorides (as NaCl), 2·38—2·68; P_2O_5, 1·31—1·58; Fe, 0·016—0·018. Nitrogen, 2·3—2·5; fat, 27·80—28·80; bile salts (sodium glycocholate and taurocholate), 15·30—15·80; nucleoprotein, 1·15—2·25; lipoids, 1·100—2·130. The latter contained cholesterol 0·410—0·813, with lecithin and neutral soaps 0·690—1·317. The livers of the same animals gave water, 689—755·20; ash free from carbon, 16·20—20·49; glycogen, 28·80—83·40; carbamide, 0·615—0·683; P_2O_5, 2·90—3·48; chlorides (as NaCl), 1·95—2·86. The figures represent parts per 1000 of fresh substance. W. O. W.

The Relationship between Nuclear Material and Development. ERNST MASING *Zeitsch. physiol. Chem.*, 1911, 75, 135—140).—The numbers given in connexion with the liver of rabbit embryos show that nucleic acid is more abundant relatively in early than in later stages. W. D. H.

Bio-chemical Relations of Various Lipoid Substances in the Liver. FREDERICK P. WILSON (*Bio.-Chem. J.*, 1911, 6, 100—105).—The acetone-insoluble fraction of the ether extract of the liver yields the most suitable antigen in the Wassermann reaction. Extracts made with cold and hot alcohol yield substances which differ from each other and from those in the ether extract in physical and biochemical properties, but these differences are apparently not dependent on the saponification or iodine values. W. D. H.

Deamidisation. GERTRUDE D. BOSTOCK (*Bio.-Chem. J.*, 1911, **6**, 48—68).—Emulsions of liver and intestinal mucosa liberate ammonia from asparagine to a less extent than from glycine and leucine, and more than from alanine. This confirms Lang's statement, but no inhibition of the deamidising enzyme was found on adding an antiseptic. In the body the nitrogen of glycine appears quantitatively as urea in the urine within eight hours, whilst only 63% of asparagine nitrogen so appears in the same time, whereas *in vitro*, ammonia is more readily liberated from asparagine than from glycine, that is, the amide nitrogen attached to the carboxyl group is more readily liberated than the amide group in the α-position. W. D. H.

The Possible Vicarious Relationship between the Pituitary and Thyroid Glands. SUTHERLAND SIMPSON and ANDREW HUNTER (*Quart. J. exp. Physiol.*, 1911, **4**, 257—272).—Complete removal of the thyroid in lambs from seven to eight months old and in adult sheep does not lead to the appearance of iodine in the pituitary even after so long an interval as five to six months. On the assumption that the active substance secreted by the thyroid is the one which contains iodine, no support is lent to the view, originally advanced by Rogowitsch, that there is a vicarious relationship between the two organs. In thyroidectomised animals the increase noted in the size of the pituitary body was not so great as has been reported by other observers.

W. D. H.

The Thyroid and Enzymatic Processes. A. J. JUSCHTSCHENKO (*Zeitsch. physiol. Chem.*, 1911, **75**, 141—168).—Removal of the thyroid in dogs and rabbits lessens the amount of catalase in all the organs investigated, including the blood; the amount of nuclease is also lessened. Administration of thyroid extract increases the catalase, the nuclease, the inorganic phosphates of the blood, the antitryptic and hæmolytic power of the serum, and the appearance in the blood of materials which, together with the antigen from the thyroid, lead to a union with complement. W. D. H.

Proteolysis in the Thymus of the Calf. NILS J. ROSS (*Zeitsch. physiol. Chem.*, 1911, **75**, 197—206).—Proteolytic changes occur more readily in the autolysing thymus if the reaction is acid than if it is alkaline or neutral. This apparently is not due, as in the spleen (Hedin), to the effect of acid in destroying an inhibitory substance. The proteolytic enzyme was obtained by perfusing the organ with 0·2% acetic acid; it is feebly antagonised by ox-serum; if the enzyme is prepared by a neutral (calcium carbonate) infusion, no such inhibition is noticed. Kaolin added in quantity sufficient to completely precipitate proteins leaves the enzyme prepared by either method largely in solution. W. D. H.

Fatty Streaks in the Tunica Intima of Arteries. OSKAR KLOTZ and M. F. MANNING (*J. Path. Bact.*, 1911, **16**, 211—220).—In this degenerative condition, which may occur in quite young people, the fat is deposited in the cells of the sub-endothelial layer, and the

endothelium may be but loosely attached; the elastic fibres also appear as though they were undergoing a fatty change, and the process may go on and involve the middle coat of the artery. The fat stained as neutral fat does; it was all dissolved out by alcohol and ether; sometimes the fat globules are anisotropic, and are therefore probably lipoid. The cause of this change, which primarily attacks the internal coat, is probably direct irritation by toxins produced by infection.

W. D. H.

Gas Production in Teleostean Fishes. W. N. F. WOODLAND (*Anat. Anzieger*, 1911, **40**, 225—242).—The structure of the swim bladder, and the very remarkable arrangements for its blood supply are described in full. In the process of oxygen secretion into the bladder, there is no hæmolysis of corpuscles, but the gas comes from what is in solution in the plasma. The use of a second rete mirabile of capillaries on the course of the returning venous blood is at present unknown.

W. D. H.

Stability of the Photogenic Material of the Lampyridæ and its Probable Chemical Nature. F. ALEX. MCDERMOTT (*J. Amer. Chem. Soc.*, 1911, **33**, 1791—1797. Compare Kastle and McDermott, Abstr., 1910, ii, 1088; McDermott, this vol., i, 396).—A further study of the photogenic compound of *Photinus pyralis* and other *Lampyridae* has shown that it is more stable towards atmospheric oxygen than is usually supposed, especially when it has been dried out of contact with the air. There can be little doubt that the luminous activity is the result of the oxidation of the photogenic compound, which is probably a lipoid (phosphatide) containing an unsaturated aliphatic radicle and an albuminous complex.

A bibliography of the subject is appended.

E. G.

Proteolytic Enzymes of Invertebrates. J. SELLIER (*Bull. stat. biol. d'Arcachon*, 1910, **13**, 67—205).—In the majority of cases, the juices are neutral or slightly acid; the acidity is insufficient for true peptic action, and in certain cases is due to amino-acids. The hepatopancreas of *Helix* and *Aplysia* has no proteolytic action. The digestive juices of crustacea, cephalopods, and worms are ereptic, readily liberating amino-acids from proteins and proteoses. The juices of gasteropod molluscs are inactive. Frequently rennetic action occurs, which runs parallel with proteolytic power. In many cases the liver appears to be an organ of absorption.

W. D. H.

The Surface-tension of Lymph. I. and II. GIUSEPPE BUGLIA (*Biochem. Zeitsch.*, 1911, **36**, 411—420, 421—434).—(1) The blood of animals four to five hours after ingestion of food, and of fasting animals showed no marked differences in either the sp. gr. or surface-tension. On the other hand, the lymph, the surface tension of which was not affected much by the ingestion of carbohydrates, showed a marked diminution after ingestion of proteins and fats (as compared with the lymph of fasting animals). The sp. gr. also is lowered, whilst the percentage of total solids increases. The fats cause a greater lowering of

surface-tension than proteins. The significance of these facts as they bear on the method of resorption of food-stuffs is discussed. The surface-tension of lymph falls markedly in the first hour after food ingestion, and does not commence to rise again even after ten hours.

(II) By the same method it was found that alcohol is rapidly absorbed both from the stomach and small intestine, and enters the general circulation through the lymph and blood capillaries. Bile salts introduced into the stomach affect the surface-tension neither of the blood nor lymph. From the small intestine, on the other hand, they are absorbed and pass without change into the blood stream and lymph. Sodium soaps are absorbed in a similar way, whereas peptone does not appear (except perhaps in very small quantities) to pass the small intestine unchanged. The rate of absorption of these various substances was also investigated, and it appears that alcohol enters the circulation most rapidly. S. B. S.

Physico-chemical Investigations on Animal Liquids. VI. Chemical Reaction of Lymph. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 273—279).—The author has determined the reaction of dog's lymph: (1) by measuring the *E.M.F.* of a couple formed of the lymph and 0·01*N*-hydrochloric acid, the two liquids being united with potassium chloride solution (compare this vol., ii, 962); (2) by observing how much alkali must be added to the lymph to give an alkalinity corresponding with $C_{H^{\cdot}} = 1 \times 10^{-9}$, or of acid to reach an acidity corresponding with $C_{OH'} = 2 \times 10^{-4}$. The second estimation is carried out with the aid of two mixtures of phosphates and phosphoric acid which have that degree of alkalinity and acidity respectively; the same amount of indicator is added to the standard solution as to the lymph, and acid or alkali is added to the latter until it acquires the same colour as the standard solution (compare Walpole, Abstr., 1910, ii, 541, 995). The dissociation constant of lymph considered as a base is from 0·3 to 2×10^{-12}, whilst the dissociation constant when it is considered as an acid is 0·6 to $1 \cdot 9 \times 10^{-14}$.

R. V. S.

Physico-chemical Investigations on Animal Liquids. VII. Chemical Reaction of Bile. G. QUAGLIARIELLO (*Atti R. Accad. Lincei*, 1911, [v], **20**, ii, 302—305. Compare preceding abstract). —The measurement of the concentrations of $H^{\cdot}$ and OH' in the bile of various animals by the electric method shows that its reaction may be practically neutral or faintly alkaline or acid, the variations being possibly due to the condition of the animal. Measured by the titration method already described, the neutralising power of the bile appears to be well marked, although less than that of lymph or blood serum; the variations are considerable. Of three cases quoted, one is neutral, one alkaline, and one acid. R. V. S.

The Behaviour of Sterile and Boiled Milk Towards Rennet and Acid. ALOIS KREIDL and EMIL LENK (*Biochem. Zeitsch.*, 1911, **36**, 357—362).—Both boiled and sterile milk clot on treatment with rennet, if either the latter or the vessels in which the experiments are

carried out are not sterilised. Sterile milk (acidity 20—22) will not clot if treated with sterile rennet in sterile vessels. Touching the mixture with a non-sterile finger, or the addition of a few drops of ordinary milk, is sufficient to cause it to clot. The lactic acid bacillus develops best in slightly acidified milk (0·2—0·6 c.c. $N/10$-acid to 10 c.c. of milk). The addition of acid to the extent even of 2 c.c. to 10 c.c. of sterile milk in sterile vessels causes no precipitation, and no additional formation of acid at incubator temperature. S. B. S.

The Influence of the Cooling of Milk on the So-called Schardinger Reaction. Robert Burri and H. Schmid (*Biochem. Zeitsch.*, 1911, **36**, 376—388).—In fresh milk, with few bacteria, the Schardinger methylene-blue–formaldehyde reaction is not an unalterable constant, but depends on the temperature at which the milk has been preserved. The reaction time is reduced by cooling the milk to 10° or lower. The same result is obtained whether the milk be cooled only to 10° or frozen. The authors have studied the conditions under which the changes produced by cooling may be made reversible. They assume that by the cooling of milk the fat is converted into two separable phases, the first being a change from the liquid to the solid condition, and the second being a change in the solid phase, whereby crystallisation processes play the main part. S. B. S.

The Ammonia of the Urine and its Relationship to Gastric Secretion. S. A. Gammeltoft (*Zeitsch. physiol. Chem.*, 1911, **75**, 57—70).—The investigations on human beings described in this paper confirm Loeb's statement, that ammonia excretion falls after a meal. This indicates that ammonia production is regulated with the object of maintaining a constant concentration of hydrogen ions in the tissues. When after a meal hydrochloric acid is absorbed, it is neutralised by ammonia. W. D. H.

Creatinine Excretion in Man Under the Influence of Muscular Tonus. Cornelis A. Pekelharing (*Zeitsch. physiol. Chem.*, 1911, **75**, 207—215 *).—The present observations on man confirm the results previously arrived at from experiments on other vertebrates, that in muscular tonus the chemical change is different from that associated with contraction. In the former case, creatine is formed as a product of nitrogenous metabolism, whereas in contraction it is non-nitrogenous substances which are utilised.

W. D. H.

Protein Metabolism of the Fœtus. The Distribution of Nitrogen in the Maternal Urine and in the Fœtal Fluids Throughout Pregnancy. Dorothy E. Lindsay (*Bio-Chem. J.*, 1911, **6**, 79—99).—The urine of the cow contains a large amount of allantoin and of hippuric acid; bullock's urine contains much less hippuric acid and amino-acids, whilst allantoin is almost entirely absent. Throughout the first half of pregnancy, the non-protein nitrogen increases in the fœtal fluids, but the amount of nitrogen per unit of weight of the fœtus decreases regularly. The fœtal fluids contain urea,

* *Proc. K. Akad. Wetensch. Amsterdam*, 1911, **14**, 310—314.

allantoin, monoamino-acids, creatinine, and creatine together with [illegible] amounts of polypeptides, diamino-acids, and contain other nitrogenous compounds (which are absent in adult urine) of undetermined nature. Throughout pregnancy the main variation in the fœtal fluids consists in a decrease in the proportion of urea and a corresponding increase of allantoin and amino-acids. The early allantoic fluid, that is, the urine of the early fœtus, shows as compared with the urine of the adult a low urea content, a high proportion of allantoin and amino-acids, and of undetermined nitrogen. The fœtal metabolism differs from that of the adult in the less complete katabolism of protein, and a greater activity of nuclear metabolism, as indicated by the amount of allantoin. The materials used in the research were obtained from sheep, oxen, and cows. W. D. H.

The Urine of Women Under Normal Conditions with Special Reference to the Presence of Creatine. R. A. Krause (*Quart. J. exp. Physiol.*, 1911, **4**, 293—304).—In women creatine is not an abnormal urinary constituent; it is always present immediately after menstruation, and often in the inter-menstrual period; it is present throughout pregnancy, and after parturition is temporarily increased. After menstruation and during pregnancy, ammonia and undetermined nitrogen increase, whilst urea diminishes in the urine. The existence of a correlation between creatinuria and the female sexual cycle also occurs in the bitch. W. D. H.

The Maximum Production of Hippuric Acid in Animals with Consideration of the Origin of Glycine in the Animal Body. A. I. Ringer (*J. Biol. Chem.*, 1911, **10**, 327—338).—Goats and rabbits have the power of eliminating hippuric acid containing more glycine than is preformed in the proteins they metabolise. As much as 38·4% of the total nitrogen of the goat is eliminated as glycine in hippuric acid. The ingestion of the benzoates increases the nitrogen eliminated, but not the urea; the increase is greater than is accounted for in hippuric acid. It is suggested that the large amount of glycine originates from the "extra destroyed" protein, and not from the protein which would have been metabolised if no benzoate had been given. The diet has no influence on the amount of hippuric acid eliminated. No synthetic production of glycine from glycollic acid could be determined. A suckling calf, fifteen days old, which had never received the glycine complex in its food, was in full possession of the power to synthesise hippuric acid and eliminate it in large quantities. W. D. H.

Are Starch Granules Excreted by the Kidneys? J. Voigt (*Biochem. Zeitsch.*, 1911, **36**, 397—400).—The author fed a normal individual on rice starch contained in a gel made from gelatin, and the urine voided during the twenty-four hours after the starch diet was examined. The various precautions taken to avoid any accidental contamination with starch granules are described in detail. He failed to find any trace of starch in the urine, a result which was not in accordance with those of Rahel Hirsch and of Verzár (this vol., ii, 744). S. B. S.

Pancreatic Diabetes in Cold-blooded Animals. VINCENZO DIAMARE (*Arch. ital. biol.*, 55. Reprint, 11 pp.).—In frogs, removal of the pancreas produces intense glycosuria, which is usually fatal within a fortnight. Mere separation of the pancreas from the intestine, provided its blood vessels are intact, does not lead to this result. Frogs can also be rendered glycosuric by hypodermic injections of dextrose; the pancreas is not thereby altered histologically. Removal of both liver and pancreas does not produce glycosuria, but the animals do not usually survive this severe operation long.

In the dog-fish (*Scyllium catulus*), extirpation of the pancreas produces hyperglycæmia, but no glycosuria. The kidney of this animal is not permeable to dextrose, and none passes into the urine even when large amounts are introduced directly into the circulation.

W. D. H.

Action of Barium and Calcium on the Heart. Extra Systolic Ventricular Tachycardia Experimentally Produced by Stimulation of the Accelerator Nerves. C. J. ROTHBERGER and HEINRICH WINTERBERG (*Pflüger's Archiv*, 1911, 142, 461—522).—One result of stimulation of the accelerator nerves of the heart in the dog is that extra beats of the ventricles are occasionally seen. After the injection of barium or calcium salts this always occurs, these salts increasing the irritability of the neuro-muscular mechanism of the heart. This occurs more readily on the left than on the right side. Strontium and magnesium salts are inactive in this direction.

W. D. H.

The Increase of Cardiac Activity Produced by Calcium. C. J. ROTHBERGER and HEINRICH WINTERBERG (*Pflüger's Archiv*, 1911, 142, 523—530).—Injection of small quantities of calcium chloride markedly increases the output of the cat's heart as measured by a stromuhr, without increasing its rate; the rate may be slightly lessened.

W. D. H.

Action of Barium Ions on the Heart. N. WERSCHININ (*Arch. exp. Path. Pharm.*, 1911, 66, 191—204).—Barium ions, like substances of the digitalis group, have a systolic and diastolic action on the frog's heart when applied endo- or exo-cardially. There is, however, a quantitative difference due to the small power the barium ions have in penetrating the outer surface of the heart; the inner surface is more permeable. The effect is easily removed by washing out with pure Ringer's solution.

W. D. H.

Biology of the Metal Thorium. ARNOLD ROSSEL (*Arch. Sci. Phys. Nat.*, 1911, [iv], 32, 347—348).—Bolton has observed that if thorium is kept in sterilised water, bacteria, which can be developed by culture on gelatin, are formed on the surface of the metal. This result was not obtained with any of the ordinary metals. The author has completed this observation as follows: Thorium was mixed with sterilised sea-sand in proportions varying from 0 to 50%. These mixtures were then placed in sea-water in separate flasks, and into each there were put twelve to fifteen examples of a simple vertebrate animal (the fish *Lanceolatus*). After five months all the fish were

dead in the flask with no thorium, and there was a thick growth of algæ. In the flask containing 50% thorium all the fish were alive and there were practically no algæ. In the intermediate flasks there was a gradation in the state of the contents. This seems to show that metal thorium is capable of destroying certain injurious germs without endangering life. W. G.

Biological Action of Thorium. WERNER VON BOLTON (*Zeitsch. Elektrochem.*, 1911, 17, 816—817).—Ordinary distilled water kept in closed sterilised vessels containing metallic thorium for six months contains micro-organisms capable of growing on nutrient media. No signs of life are found after one year. Comparative experiments with other metals showed no signs of life at all.

Amphioxus kept in well aerated sea-water containing sea-sand, or mixtures of sand and thorium, died in five weeks with sand alone; with 10% of thorium, 10% of the fish were alive after three months; with 25% of thorium, 30% of the fish survived this time, whereas with 50% of thorium, 90% of the fish were still alive after seven months. Thorium oxide had a very much weaker effect.

The effect on the growth of plants of mixing from 10 to 50% of thorium with soil is also studied. Seeds germinate some days later, and the young plants die when half developed in the soil containing the metal. T. E.

Investigations with Mesothorium on Animal Germ Cells: an Experimental Proof of the Idioplasmic Nature of the Nuclear Material. OSCAR HERTWIG (*Sitzungsber. K. Akad. Wiss. Berlin*, 1911, 39, 844—873).—Previous work by the author has shown that exposure of the male and female germ cells to the influence of radium emanations does not kill the cells, but when impregnation occurs, development is slowed, and gives rise to imperfect and distorted larvæ. This effect is more marked the longer the exposure. Histological and other evidence is adduced to show that the emanations produce their effect by injuring the nuclei. The theory that the harm is produced by toxic products liberated by the cleavage of lecithin is discussed, but not agreed with. The present research continues and amplifies these conclusions by further experiments on the generative cells of frogs. The material used was mesothorium, the radio-activity in the specimens used being eight times greater than that of the radium bromide used in the previous experiments. The effects are much more pronounced. Exposure to the rays from fifteen to thirty seconds produces a marked effect, an effect the sensitiveness of which is compared to that of light on a photographic plate. The experiments confirm the doctrine that the nucleus has an idioplasmic nature, that is, contains the hereditary elements; objections to this view are discussed at length. W. D. H.

The Action of Cholesterol and its Derivatives with Lecithin as Syphilitic Antigen and as Hæmolysin with Cobra Venom. CARL H. BROWNING and JOHN CRUICKSHANK (*J. Path. Bact.*, 1911, 16, 225—246).—A full account of a research of which a preliminary notice has already appeared (this vol., ii, 1014). W. D. H.

Pharmacological Properties of Certain Acid Oxidation Products of Cholesterol. FERDINAND FLURY (*Arch. exp. Path. Pharm.*, 1911, 66, 221—237).—The acids with formulæ $C_{27}H_{44}O_6$, $C_{27}H_{40}O_5$, and $C_{27}H_{40}O_4$ (compare Windaus, Abstr., 1908, i, 264) are strongly toxic, and are physiologically related to the pharmacological group of the bile acids and saponins. They are absorbed with difficulty, produce local necrosis of tissues, paralysis of skeletal and cardiac muscle, slowing of the heart, and intense hæmolysis. In such properties they also closely resemble certain snake venoms, especially viper-venom. They may perhaps be intermediate products in the formation of bile acids from cholesterol, and formed in small amount may normally be important in the maintenance of muscular tonus.

W. D. H.

Physiological Action of Iodo-fatty Acid Derivatives. EMIL ABDERHALDEN and PAUL HIRSCH (*Zeitsch. physiol. Chem.*, 1911, 75, 38—56).—See this vol., i, 954.

Influence of Chemical Constitution on the Toxicity of Nitriles and Amides. ALEXANDRE DESGREZ (*Compt. rend.*, 1911, 153, 895—898. Compare this vol., ii, 756).—Comparison of the toxic power of a number of saturated nitriles and the corresponding unsaturated compounds towards rabbits and guinea pigs has shown that double or triple linkings increase the toxicity. A similar generalisation holds good for amides, and hence it is unnecessary to suppose that the great toxicity of unsaturated nitriles, such as the cyanoacetylenes previously studied, is due to fixation of water followed by liberation of hydrogen cyanide. The difference is less marked between saturated and unsaturated compounds in the aromatic series than in the aliphatic. Generally speaking, toxicity increases with the molecular weight, but the aromatic compounds are more poisonous than aliphatic substances of about the same molecular weight.

W. O. W.

The Action of Nucleic Acid on the Fermentative Processes in the Animal Body. M. TSCHERNORUZKI (*Biochem. Zeitsch.*, 1911, 36, 363—375).—The sodium salt of yeast-nucleic acid (Merck's preparation) was administered in various ways (subcutaneously, *per os*, and intravenously) to a number of puppies from the same litter. One other animal received no treatment, and was kept as a control. The nucleate, even in large doses (1·5 grams to a kilo. of body-weight), exerted no injurious effect. At the end of a given period, after repeated administrations, the animals were killed, and the organs were removed from the body and dried at low temperatures. The amounts of the various ferments in the different organs were then estimated by the usual methods, and the results obtained in the treated animals compared with those from the control animal. The chief changes were observed in the brains, lungs, muscles, and thymus. In the case of the brain, the amylase was found to be 400 times greater than the normal, the diastase 4·4 times greater, and the protease 10 times. In the lungs, the diastase was 250 times greater than normal, and

6·4 times greater in the muscles. The results for other ferments and organs were not sufficiently definite for generalisation.

S. B. S.

Pharmacological Properties of Adaline (α-Bromo-α-ethyl-butyrylcarbamide). EDUARDO FILIPPI (*Arch. Farm. sper.* 1911, 12. Reprint 10 pp. Compare Impens, *Med. Klin.* Woch., No. 47).—Adaline is a sedative producing light, but lasting, sleep; it exerts no cardiac action, and its toxicity (for rabbits) is very small. Pancreatic extract dissolves the substance somewhat readily. The urine of animals (rabbits, dog) to which the substance has been administered contains some of it unaltered, but the urine also yields an *acid*, which forms acicular crystals, m. p. 87—89°, and contains bromine. Ionic bromine appears in the urine only in cases of severe poisoning.

R. V. S.

Pharmacology of the Bronchial Musculature. HANS JANUSCHKE and LEO POLLAK (*Arch. exp. Path. Pharm.*, 1911, 66, 205—220).—Intravenous injection of adrenaline increases the respiratory excursions of the lungs, especially when muscarine asthma has been induced. The latter is due to cramp of the bronchial muscles, and this is antagonised by adrenaline. Bronchial spasm produced by injection of peptone (but not that produced by β-iminazolylethylamine [4-β-aminoethylglyoxaline] or ergotoxine) is also inhibited by adrenaline.

W. D. H.

Physiological Action of β-Aminoethylindole. PATRICK P. LAIDLAW (*Bio.-Chem. J.*, 1911, 6, 141—150).—β-Aminoethylindole is formed from tryptophan by bacterial action. It exerts a transient stimulant effect on the central nervous system, and has also a direct stimulant action on plain muscle, especially of the iris, uterus, and arterioles.

W. D. H.

Pharmacology of Veronal. I. Symptoms and Doses. CARL ROEMER (*Arch. exp. Path. Pharm.*, 1911, 66, 241—260).—A general account of the effects of veronal in frogs, rabbits, and cats, especially when used in fatal doses. The minimal fatal dose for the frog is 1·5 grams, for the rabbit 0·4 gram, and for the cat 0·3 to 0·35 gram per kilo. of body-weight.

W. D. H.

Pharmacology of Veronal. II. Influence on Temperature, Breathing, and Circulation. CARL JACOBJ and CARL ROEMER (*Arch. exp. Path. Pharm.*, 1911, 66, 261—295).—Veronal lowers the body temperature, somewhat slows the rate of breathing while increasing its depth, and lowers blood pressure by dilating peripheral vessels. The effect on the vessels appears to be mainly due to a local action of the drug. Larger doses are needed to affect the isolated frog's heart.

W. D. H.

Pharmacology of Veronal. III. Action of Veronal in Reference to its Specific Paralytic Action on the Vessel Walls. CARL JACOBJ (*Arch. exp. Path. Pharm.*, 1911, 66, 296—31.).—This is largely a commentary on the preceding papers, written

mainly from the therapeutic point of view. The use of the drug is contra-indicated in cases where dilatation of the vessels should be avoided, for instance, in diseases of the kidney associated with venous congestion. W. D. H.

Chemistry of Vegetable Physiology and Agriculture.

The Action of Certain Bacteria on Proteins. FRANCIS A. BAINBRIDGE (*J. Hygiene*, 1911, **11**, 341—355).—When solutions of pure egg-albumin, serum-protein, or alkali-albumin are inoculated with the organisms, *B. coli*, *B. enteritidis*, *B. typhosus*, *B. proteus*, *B. pyocyaneus*, *Staphylococcus p. aureus*, and *Gonococcus*, the bacteria diminish in number when the seeding is large, but multiply to some extent when the seeding is small. The latter effect is probably due to non-protein nitrogenous substances, and not to the fact that bacteria use the protein as food. If any protein is used, it must be the smallest traces. The organisms examined (with the exception of *B. proteus*) do not break down appreciable quantities of egg- and serum protein, even in the presence of sufficient non-protein nitrogenous food to ensure vigorous growth. W. D. H.

The Decomposing Power of Water Bacteria. WILHELM SPÄT (*Arch. Hygiene*, 1911, **74**, 237—288).—The amount of ammonia formed when 0·2 c.c. of a sample of water is added to 100 c.c. of 2% peptone solution, and incubation allowed to proceed at 37° for twenty-four hours, may serve as a criterion of the purity of the sample employed. The amount of decomposition does not bear any direct relation to the absolute number of bacteria, since those normally present in water are able to ammonify peptone only to a slight extent; this also applies to *Bacterium coli* and to pathogenic organisms generally. Contamination of the water by surface drainage introduces physiologically active soil bacteria, and is reflected in a greatly increased decomposing power of the sample in the majority of the cases investigated. Storage does not affect the decomposing power of the water, so that ice-cooling during transit of the sample is unnecessary. H. B. H.

The Action on Nitrates and Nitrites of Dysentery Organisms. W. J. LOGIE (*J. Hygiene*, 1911, **11**, 361—372. Compare Abstr., 1910, ii, 988).—The organisms examined were killed (1) by temperatures which should not have destroyed the reducing enzyme; (2) by sodium fluoride and four other antiseptics, derivatives of phenol mentioned below, and (3) by acetone. In each case there was total destruction of the reducing power. Filtrates of fluid cultures have also failed to reduce nitrates to nitrites. The reduction cannot, therefore, be due to a soluble extra-cellular enzyme. The high antiseptic value of tetrachloro-*o*-diphenol, tetrabromo-*o*-cresol, *p*-chloro-*m*-cresol, and

hexabromodihydroxydiphenylcarbinol is established for [illegible] organisms. W. D. H.

Sugar Tests and Pathogenicity in the Differentiation of Streptococci. J. M. BEATTIE and A. G. YATES (*J. Path.* [illegible] 1911, 16, 247—256).—A full account of a research of which a preliminary notice has already appeared (this vol., ii, 1019). W. D. H.

The Mechanism of Alcoholic Fermentation. A[illegible] LEBEDEFF (*Ber.*, 1911, 44, 2932—2942; *Bull. Soc. chim.*, [iv], 9, [illegible]).—A detailed description of the experimental evidence on which is founded the theory of alcoholic fermentation already given (Abstr., 1911, ii, 816). W. J. Y.

Alcoholic Fermentation. HARTWIG FRANZEN and O. STEPPUHN (*Ber.*, 1911, 44, 2915—2919).—The action of yeast on formic acid was determined by growing pure cultures in sterile beer-wort containing 0·01 molar sodium formate, and estimating the formic acid present at daily intervals. In most cases it was found that considerable quantities of formic acid disappeared. In several cases, however, a formation of this substance occurred during the early stages of the growth, which was followed by a gradual decrease as time went on. It was further found that when no formate was originally present in the wort, formic acid was first formed and then gradually fermented. The formic acid cannot all be derived from the alcoholic fermentation of amino-acids, since the quantity found was greatly in excess of that corresponding with the amyl alcohol and succinic acid produced in the fermentations.

The conclusion is drawn that it is formed as an intermediate product in the alcoholic fermentation of the sugar of the wort, the quantity found representing the balance between the amount formed and that fermented.

These experiments thus lend support to the theory of alcoholic fermentation of Wohl as elaborated by Schade, according to which lactic acid is formed from the sugar, and is then converted into acetaldehyde and formic acid, which react together to form carbon dioxide and alcohol. W. J. Y.

The Formation of Plasma Protein by Yeasts and Moulds. FELIX EHRLICH (*Biochem. Zeitsch.*, 1911, 36, 477—49[illegible]).—It has been shown by the author and his co-workers that when yeasts, etc., act on amino-acids, alcohols, such as amyl alcohol, tyrosol, etc., are produced (according to the amino-acid used in the experiment), and that the amount of destruction of the amino-acid is proportional to the amount of alcoholic fermentation. The conclusion is drawn from the results, that the alcohols, such as amyl alcohol or tyrosol, which are derived from the amino-acids are merely waste products, and form no direct part in the protein synthesis of the yeast, which merely uses the ammonia set free. The latter substance acts on the degradation products of the dextrose only, to form the amino-acids which are concerned in the synthesis of the plasma protein. Experiments were

therefore carried out to determine whether yeast would grow in the presence of sugar degradation products only, with tyrosine as the source of nitrogen. This substance yields as reaction product either tyrosol or *p*-hydroxyphenyl-lactic acid, according to the mould used in the experiment. Both these substances can be readily isolated, and the ratio between the amounts isolated and the protein nitrogen formed in the yeast growth was estimated. Tartaric, lactic, and formic acids (as sodium salts), glycerol, methyl and ethyl alcohols were the degradation products of sugar employed. In the case of yeast the results were negative, but this was not so in the case of certain "wild" yeasts and moulds which were employed, namely, *Willia anomala*, Hansen, and *Oidium lactis*. The former yielded tyrosol, whereas the latter yielded *p*-hydroxyphenyl-lactic acid. Positive results were obtained with ethyl alcohol and glycerol, and, to a small extent, with methyl alcohol, and the amount of nitrogen in the culture was, in the case of the *Willia anomala*, more or less proportional to the amount of tyrosol recovered. In the case of the *Oidium lactis* positive results were also obtained with sodium lactate. Preliminary experiments carried out in a similar way with pyruvic acid also yielded positive results with *Willia anomala* and a brewer's yeast, although the latter only developed slowly in the artificial culture medium. S. B. S.

The Anti-bactericidal Action of the Bile Salts. S. Lyle Cummins (*J. Hygiene*, 1911, 11, 373—380).—Sodium taurocholate and glycocholate possess anti-bactericidal qualities; glycine, taurine, and cholic acid have not. This explains why the addition of bile salts to culture media, such as serum, increases the growth of the typhoid bacillus. The action depends on interference with the complement, and not on inhibition of the action of the amboceptor. The action of bile may explain the survival of the bacilli in typhoid carriers.

W. D. H.

Increasing the Activity of Higher and Lower Plants by Small Amounts of Poisons. Edwin Broun Fred (*Centr. Bakt. Par.*, 1911, ii, 185—245).—Ether, carbon disulphide, potassium dichromate, and copper sulphate promote the growth of lower organisms when sufficiently dilute solutions are employed. The organisms included *Azotobacter*, dinitrifying, ammonia, and putrefactive bacteria, and yeasts. In presence of ether, the fixation of nitrogen by *Azotobacter* in mixed cultures is increased; with pure cultures, fixation of nitrogen is increased by ether and carbon disulphide, but not to the same extent as with mixed cultures. The growth of denitrifying organisms is slightly increased by antiseptics.

Application of ether to soil at first retards nitrification; subsequently nitrification is considerably increased. Experiments with plants showed that ether and carbon disulphide increase the growth.

The conclusion is drawn that the beneficial effect of these substances is due to their stimulating action on the plants and on soil organisms.

N. H. J. M.

Action of Ether and Carbon Disulphide on Higher and Lower Plants. ALFRED KOCH (*Centr. Bakt. Par.*, 1911, ii, 31, 175—185).—The results of pot experiments in which wheat, followed by mustard, were grown in soil to which ether was applied, and in the same soil without ether, showed that the yield of wheat and the nitrogen assimilated were doubled under the influence of ether, whilst the second crop (mustard) was somewhat less than in the check pots.

Small amounts of ether have a retarding action on nitrification followed by a slight increase. The conclusion is drawn that the increased yields obtained after the application of ether or carbon disulphide cannot be due to increased nitrification or diminished dinitrification, but to stimulation of the higher plants.

The results of fermentation experiments showed that small amounts of ether increase the activity of yeast. Carbon disulphide gave negative results (compare Goemer, *Koch's Jahresber*, 2, 169).

N. H. J. M.

The Wandering of Betaine in Certain Vegetative Processes in Plants. VLADIMIR STANĚK (*Zeitsch. physiol. Chem.*, 1911, 75, 262—271).—The dry residue of young leaves contains more betaine and more total nitrogen than old leaves. In the ripening of plant organs, betaine diffuses simultaneously with other nitrogenous substances. It is probably not a katabolic product, and trimethylamine is never found.

Betaine is formed during germination of the seed, and it is difficult to say whether it originates from reserve materials or in assimilated nitrogenous substances. During sprouting the betaine collects in the leaves, but it plays no part in the action of light on etiolised leaves, nor in the assimilation of carbon.

W. D. H.

Enzymic Degradation of Arginine in Plants. ALEXANDER KIESEL (*Zeitsch. physiol. Chem.*, 1911, 75, 169—196).—Arginine may be decomposed by ferments into ornithine and carbamide, or oxidised to give γ-guanidinobutyric acid, or with the loss of carbon dioxide to agmatine, $NH_2 \cdot C(NH) \cdot NH \cdot [CH_2]_4 \cdot NH_2$. Each of these products may conceivably undergo further decomposition.

An attempt has been made to establish the manner of the decomposition of arginine in plants; it is proved that the change, although not quantitative, consists for the great part in the conversion into ornithine and urea. The formation of neither agmatine nor guanidine could be detected. The absence of guanidine is not due to any possibility of its removal by secondary changes; this point is still being investigated in the case of agmatine. Agmatine could not be obtained on hydrolysis of wheat embryos or by the autolysis of yeast.

The fact that ornithine has not yet been found in plants is not due to its removal by further change, but probably to the inadequate methods of isolation and identification when it is present in an impure condition. The formation of putrescine as a decomposition product of ornithine could not be detected. Plants contain a ferment (urease)

which decomposes carbamide as rapidly as it is formed, so that carbamide can only be found in those plants which lack this enzyme. Wheat embryos contain a very active urease. Urease is very specific in its action, and does not act synthetically. E. F. A.

Formation of Anthocyanic Pigments. RAOUL COMBES (*Compt. rend.*, 1911, **153**, 886—889).—A preliminary note recording the isolation from autumnal leaves of *Ampelopsis hederacea* of a pigment crystallising in clusters of purple needles. The substance is very soluble in alcohol, sparingly so in water, ether, and benzene, and forms a green compound with lead acetate. Green leaves of the same plant yielded a substance crystallising in brown needles, and forming a yellow compound with lead acetate. The red colour of the autumn leaves is probably due to the first-mentioned pigment, which is related to the second in the manner suggested in an earlier paper (Abstr., 1909, ii, 426). W. O. W.

Manganese in Digitalis purpurea. JAMES BURMANN (*Bull. Soc. chim.*, 1911, [iv], **9**, 957—959).—*Digitalis ambigua* and *D. lutea* are indigenous to Switzerland, whilst *D. purpurea* can only be grown in gardens and does not reproduce itself. This seems to be due to the fact that the two former do not require manganese, whilst the third species does. Digitalis leaves grown on soil derived from ferruginous grit in Alsace gave 5·08% of ash, containing 9·02% manganese and 0·80% iron, whilst the grit itself contained 0·43% manganese and 4·82% iron. The presence of manganese in the ash serves to distinguish *D. purpurea* from *D. ambigua* and *D. lutea*. T. A. H.

Green and Yellow Dyes of Florideæ. LEON MARCHLEWSKI (*Zeitsch. physiol. Chem.*, 1911, **75**, 272. Compare Kylin, this vol., ii, 1024).—Kylin was unable to isolate chlorophyllanic acid and *allo*-chlorophyllanic acid from his material; these substances are best identified by conversion into phyllocyanin and phylloxanthin.

E. F. A.

Hydnocarpus Fats. K. LENDRICH, E. KOCH, and L. SCHWARZ (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 441—458. Compare Power and Gornall, Proc., 1904, **20**, 137; Trans., 1904, **85**, 838, 851; Power and Barrowcliff, Trans., 1905, **87**, 884, 896).—Margarine made with a so-called "cardamom oil" from India having caused several cases of illness, the margarine and the "cardamom oil" have been examined chemically and physiologically with the view of identifying the botanical source of the oil and to ascertaining the cause of its toxicity. The oil is probably derived from the seeds of either *Hydnocarpus Wightiana* or *H. venenata*, and owes its physiological action to the presence of chaulmoogric and hydnocarpic acids (compare Litterscheid, *Chem. Zeit.*, 1911, **35**, 9; Reinsch, *Chem. Zeit.*, 1911, **35**, 77; Thoms and Müller, *Zeitsch. Nahr. Genussm.*, 1911, **21**, 226; Plücker, *ibid.*, 1911, **21**, 257).

The "cardamom" oil had D 0·9549—0·9560, m. p. 23·3—23·8°,

acid number 9·3—20·5, saponification number 202·6—[illegible], iodine number 92·4—96·9, $[\alpha]_D^{20}$ +54·67° in 50% or +55·02° in 10% benzene solution. *Hydnocarpus Wightiana* fat had acid number 12·0, saponification number 203·9, iodine number 100·7, $[\alpha]_D^{20}$ +55·6°. *H. venenata* fat had acid number 44·0, saponification number 202·4, iodine number 97·0, $[\alpha]_D^{20}$ +55·9°. *H. inebrians* fat had saponification number [illegible], iodine number 80·9, $[\alpha]_D^{20}$ +42·3°. *H. anthelmintica* fat had acid number 12·0, saponification number 209·8, iodine number [illegible], $[\alpha]_D^{20}$ +51·5°. *Taraktogenos Kurzii* fat had saponification number [illegible], iodine number 89·1, $[\alpha]_D^{20}$ +47·7° (compare Power and collaborators, *loc. cit.*). The "cardamom" oil furnished chaulmoogric and hydnocarpic acids identical with those isolated by Power, Gornall, and Barrowcliff from the fats of *Taraktogenos Kurzii* and *Hydnocarpus anthelmintica* (Trans., 1904, 85, 838; 1905, 87, 884), but, unlike these fats, yielded no palmitic acid, in which respect it resembles the *H. Wightiana* fat examined by Power and Barrowcliff (*loc. cit.*, p. 884). The "cardamom" oil produced nausea and sickness in dogs, as did also the chaulmoogric, hydnocarpic and liquid fatty acids isolated from it. The oxidised or brominated total fatty acids of the oil, however, proved to be physiologically inactive. All the *Hydnocarpus* fats and the *Taraktogenos Kurzii* fats also produced sickness in dogs. The toxic symptoms observed in all cases were vomiting and irritation of the mucous membrane of the stomach, with in some cases clonic convulsions of the whole body. This physiological action appears to be correlated with the presence of an ethylene linking in the optically active acids of this group of fats, since the oxidised or brominated acids are inactive.

Hydnocarpus alpina fat had acid number 5·6, saponification number 209·06, iodine number 84·5, $[\alpha]_D^{20}$ +49·0°, and is probably quite similar to the other fats of this genus examined (compare Grimme, *Chem. Rev. Fett. u. Harz.*, 1911, 18, Part 7). T. A. H.

Shea Butter. Alexandre Hébert (*Bull. Soc. chim.*, 1911, [iv], 9, 959—963. Compare Southcombe, Abstr., 1909, ii, 604).—Shea butter (Fr. karité butter) yields 96% of total fatty acids, m. p. 51°, containing 33% of oleic acid and 67% of saturated acids composed of arachidic, stearic, and palmitic acids. There is no material difference in the yield or characters of the fats derived from sun- or kiln-dried kernels (compare *Bull. Imp. Inst.*, 1908, 6, 369).

T. A. H.

Experimental Chlorosis of Maize. Pierre Mazé (*Compt. rend.*, 1911, 153, 902—905).—Maize grown in nutrient solutions free from iron or sulphur develops a very thin, almost transparent parenchyma, and the leaves do not become green. Deprivation of chlorine, magnesium, or silicon does not have this effect. That iron and sulphur are assimilated and fixed by the cells is shown by the fact that leaves etiolated in iron- or sulphur-free solutions are turned green by drops of ammonium sulphate or ferric nitrate respectively, but only in the immediate neighbourhood of the drops. W. O. W.

The Carbohydrates of the Foliage Leaf of the Snowdrop (Galanthus nivalis) and their Bearing on the First Sugar of Photosynthesis. JOHN PARKIN (*Bio-Chem. J.*, 1911, **6**, 1—47).—The total carbohydrates in the leaf amount to 20—30% of the dry weight. Starch and maltose are absent; sucrose, dextrose, and lævulose are present. The variations described in the relative amount of the three sugars occur in relation to time of day and season of the year, but the main fluctuation is in the sucrose. If the leaves are largely depleted of their sugars by darkness, the hexoses are not increased by exposure to sunlight, the augmentation being almost solely in the sucrose. The last-named sugar is regarded as the first sugar to appear, the others being derived from it by inversion; the lævulose is always in excess of the dextrose, because the latter is more immediately utilised by the leaf. This view that the first sugar to arise in photosynthesis is sucrose was first advanced by Brown and Morris, but raises a difficulty, which is discussed in full, if the current formaldehyde theory is correct. W. D. H.

The Cyanogen Compounds of Tobacco Smoke. JULIUS TÓTH (*Chem. Zeit.*, 1911, **35**, 1262. Compare this vol., ii, 143).—In reply to private enquiries, the author states that having reconsidered the process given for the estimation of cyanogen compounds in tobacco smoke (Abstr., 1910, ii, 443) he comes to the following conclusions: (1) The assumption that the conversion of cyanogen into ferrocyanide by means of potassium hydroxide and ferrous sulphate is a complete one is quite correct. (2) In consequence, it is quite certain that tobacco smoke contains more cyanogen compounds than hitherto supposed. L. DE K.

Effect of Chemical Reagents on the Respiration and Growth of Wheat Seedlings. H. S. REED (*Bied. Zentr.*, 1911, **40**, 716; from *Bot. Gaz.*, 1910, **49**, 81; *Bot. Zentr.*, 1911, 204).—Small amounts of calcium and sodium phosphate increase, whilst potassium salts diminish, respiration; sodium nitrate generally increases respiration, but its effect varies.

Respiration is diminished by inorganic acids, whilst the effect of organic acids is variable. Pyrogallol and tannic acid increase respiration considerably. N. H. J. M.

The Disease Causing Bitterness in Wines in Connexion with the Acrylic Fermentation of Glycerol. E. VOISENET (*Compt. rend.*, 1911, **153**, 898—900. Compare Abstr., 1909, ii, 738, 909).—The presence of acraldehyde in wines which have developed bitterness has been demonstrated previously, and its formation attributed to the dehydration of glycerol by a specific ferment. The bitter taste of such wines appears to be due to condensation products of acraldehyde. These substances are of a resinous character, and are produced when a dilute solution of acraldehyde is warmed with potassium hydrogen tartrate; the ferment producing the aldehyde is also capable of effecting resinification. These observations render

unnecessary Wortmann's theory that bitterness is caused by the action of oxydases on tannin and colouring matters.

W. O. W.

Effect of Soluble Salts on the Adsorption of Phosphates by Soils. HARRISON E. PATTEN (*J. Physical Chem.*, 1911, 15, 639—658. Compare Abstr., 1908, ii, 126).—The rate of extraction of phosphoric acid from superphosphated soils is increased by the presence of dissolved salts in the percolating water. The soils examined were quartz flour (83% silt, 17% clay), "Podunk" fine sandy loam, and "Elkton" clay. To each kilo. of soil was added 0·61 gram of calcium monophosphate, $CaH_4(PO_4)_2$, this being equivalent to 350 lb. per acre (depth not stated).

In the case of quartz flour the amount of phosphoric acid dissolved out by distilled water was large at first (93 parts per million), but rapidly diminished to a constant low value of about 6 parts. On substituting 0·05% sodium nitrate solution for the distilled water without interrupting the continuity of the percolation, the concentration of phosphoric acid immediately rose to 44 parts per million and remained constant. The rates of percolation of distilled water and sodium nitrate solution were approximately equal.

With the "Podunk" loam and "Elkton" clay such marked increases in the phosphoric acid concentration were not generally observed, since the rate of percolation of the salt solution was almost invariably higher than that of distilled water. Potassium carbonate solution produced a deflocculation of the loam, which became clogged and stopped the passage of the liquid.

The author draws the conclusion that higher concentrations of phosphate may be obtained when weak solutions of the salts ordinarily used as soil amendments (potassium chloride, sulphate, nitrate and carbonate, and sodium nitrate) are passed through the soil than can be obtained by the use of distilled water alone. The effect is mainly produced by the mutual interference of the adsorptions of added salt and superphosphate by the soil particles.

R. J. C.

[Amount of Nitrogen as Ammonia and as Nitrates in Rain-water Collected at Uithuizermeeden.] J. HUDIG and H. WELT (*Verslag. landbouwkund. onderzoek. Rijkslandbouwproefstat.* 1911, No. 10, 188—118).—Nitrogen in the forms of ammonia and nitrates was estimated in the rain-water collected at Uithuizermeeden, Groningen, from September, 1901, to August, 1910. The average amounts of rain and of nitrogen in the two forms were as follows:

	Nitrogen per million		Nitrogen per acre (lb.)		
Rainfall, inches.	as ammonia.	as nitrates.	as ammonia.	as nitrates.	Total.
26·20	0·724	0·237	4·301	1·407	5·708

N. H. J. M.

Analytical Chemistry.

The Sodium Phosphate Standards of Acidity. EDMUND B. R. PRIDEAUX (*Bio.-Chem. J.*, 1911, **6**, 122—126).—The H' ion concentrations obtained by mixing sodium hydroxide and phosphoric acid in varying proportions are represented graphically. Most of the results have already been published (compare Trans., 1911, **99**, 1224). The effect of errors in determining the concentrations of the reagents, and the influence of carbon dioxide have been measured. The reproducibility of the monohydrogen phosphate (Na_2HPO_4) standard from crystalline salt was found to be accurate, provided the salt is recrystallised under definite conditions. G. S.

Rapid Electroanalysis with Stirring by Bubbling a Gas Through the Solution. FRANZ FISCHER, CARL THIELE, and EMIL STECHER (*Zeitsch. Elektrochem.*, 1911, **17**, 905—906).—Instead of using a mechanical stirrer, the same object is advantageously effected by bubbling hydrogen through the electrolyte. The electrolytic cell consists essentially of a wide cylindrical glass tube, in which the cathode is supported at some distance from the bottom. The hydrogen is introduced by means of a long glass tube ending in a bulb provided with a number of small holes; the tube is so placed that the bulb is near the bottom of the cell. The cell is loosely closed by means of a funnel placed in the neck. As the electrolysis is conveniently carried out at 60°, the vapour from the solution condenses on the inner wall of the cell, and washes down any electrolyte which may be carried up on the walls by the stream of gas. It is shown that the method gives accurate results. G. S.

Rapid Electroanalysis under Reduced Pressure. FRANZ FISCHER, CARL THIELE, and EMIL STECHER (*Zeitsch. Elektrochem.*, 1911, **17**, 906—908. Compare preceding abstract).—The stirring of the electrolyte may also be effected by carrying out the experiment under reduced pressure, the volume of the gas given off during the electrolysis being thereby greatly increased. The apparatus, which is described and figured, is similar to that discussed in the former paper, except that the cell is closed by a rubber cork through which the connexions pass, as well as a glass tube connected to an ordinary filter pump. G. S.

Physico-chemical Volumetric Analysis. III. Precipitation Followed by Alteration in Potential. PAUL DUTOIT and GOTTFRIED VON WEISSE (*J. Chim. phys.*, 1911, **9**, 578—607. Compare Abstr., 1910, ii, 342).—The contact potential of a metallic electrode undergoes a sudden change at the moment the last traces of the most electropositive metal in the solution are removed by precipitation. In order to render this phenomenon available in volumetric analysis, a very small current is passed through the solution, using platinum

electrodes, and the potential between the rapidly rotating cathode and an auxiliary calomel electrode is continuously noted during the introduction of the precipitant from a burette.

When the burette readings are plotted against the voltage, the end point of the titration corresponds with a double inflexion ... curve. This inflexion point, even if well marked, may differ from the theoretical end point by as much as 10%.

Foreign substances in some cases, not only affect the ab... value of the voltages obtained, but may also displace the inflexion ... the polarisation current is long continued, or of too high a ... amount of metal is apparently electro-deposited out of all ... to the electro-chemical equivalent. The errors are such as ... through the absorption of the solution by the precipitate.

Precipitates arranged in order of increasing absorbing ... silver bromide, copper sulphide, zinc sulphide, silver ... silver iodide, silver ferrocyanide, copper ferrocyanide. The precipitation of the last-mentioned substance is the most susceptible to experimental conditions.

In each case the most favourable concentrations of solution and precipitant, and the minimum current density with which a good inflexion point is obtainable, must be predetermined, and the titration must be carried out as quickly as possible. R. J. C.

Physico-chemical Volumetric Analysis. V. Estimation and Separation of the Halogens. Paul Dutoit and G... von Weisse (*J. Chim. phys.*, 1911, **9**, 630—640. Compare B..., Abstr., 1893, ii, 387).—The use of the electrometric method instead of an indicator in the estimation of halogens has the advantage that very dilute solutions can be titrated accurately. Using silver nitrate as precipitant, 15 mg. of chloride can be estimated in a litre, and with bromide and iodide yet smaller quantities.

The alteration of potential on removing silver iodide is greater than occurs with the more soluble bromide or chloride. Iodide may be estimated in presence of an enormous excess of chloride or bromide provided that the solution is vigorously stirred to prevent premature precipitation of chloride or bromide. Chloride cannot be distinguished from bromide, as there is no marked potential change at the end of the precipitation of the bromide.

The method has been applied to the estimation of traces of chloride in potassium chlorate, and the estimation of iodine in urine. In the latter case very small quantities of iodide cannot be detected, being masked by the colloidal substances present. R. J. C.

Use of Carbon Disulphide for the Direct Estimation of Free Sulphur in Minerals. Nathan Lévy-W. (*Bull. Assoc. chim. Sucr. dist.*, 1911, **29**, [iv], 218—220).—The author uses carbon disulphide for the assay of sulphur deposits containing mineral matter (sand). The difficulty is, however, to evaporate the solvent completely without violent spirting towards the end of the operation; spontaneous evaporation is very tedious, and has other drawbacks. The author now operates as follows: The carbon disulphide containing the sulphur

from one gram of the sample is filtered into a long tube containing a little water, and, of course, collects at the bottom. The tube is now placed, in an inclined position, in a water-bath, and the carbon disulphide is completely distilled off. The vapours pass through a long, doubly bent tube, which dips into a vessel containing water, where the carbon disulphide is recovered. A small bulb with which the tube is furnished prevents regurgitation.

The sulphur is now transferred to a weighed filter, which is then washed, dried, and re-weighed.

L. DE K.

The Volumetric Estimation of Sulphur in Iron and Steel. T. GIFFORD ELLIOT (*J. Iron Steel Inst.*, 1911, 83, 412—420).—Many specimens of iron and steel do not evolve the whole of their sulphur when treated with concentrated hydrochloric acid after annealing in hydrogen. Better results are obtained by the following method, which is applicable to all varieties of iron and steel, except those containing titanium. Five grams of the drillings are mixed with 0·25 gram of dry, powdered potassium ferrocyanide, wrapped in a 11 cm. filter paper if a grey iron, or in two such papers if a white iron or steel, and annealed for twenty minutes at 750—850° in a porcelain crucible. The mass, enclosed in the charred paper, is broken up and introduced into the evolution flask, covered with 50 c.c. of hydrochloric acid, D 1·19, and heated. The absorbing solution is made by dissolving 20 grams of cadmium chloride in water with a few drops of hydrochloric acid, adding ammonia until the precipitate completely dissolves, and acidifying with acetic acid, then adding a further 20 c.c. of acetic acid, and making up to 2 litres. Sixty c.c. of this solution are used for each estimation. When no more gas is evolved, an excess of iodine solution is added to the absorbing vessel, followed by hydrochloric acid until the cadmium sulphide is dissolved. The iodine is then titrated with sodium thiosulphate.

C. H. D.

Detection of Nitrogen in Organic Substances. A. HALENKE and M. KLING (*Chem. Zeit.*, 1911, 35, 1180).—The substance to be tested is mixed with potassium hydroxide and placed in a test-tube. To the mouth of the tube is attached a Fresenius filter-tube, the bulb of which is filled with glass beads, placed over a pad of glass wool. A strip of moist red litmus paper is suspended from a hook in the upper part of the filter-tube, and the whole is connected with a vacuum pump. The test-tube is then heated slowly until the potassium hydroxide fuses. Any potassium hydroxide sprayed up is retained by the beads; therefore, if the evolved vapours turn the paper blue, ammonia must be present.

L. DE K.

Decomposition of Uric Acid by means of Dilute Sodium Hydroxide Solutions. CLARENCE E. MAY (*J. Amer. Chem. Soc.*, 1911, 33, 1783—1787).—In view of Steel's modification of Folin's method for the estimation of ammonia in urine (this vol., ii, 68), in which a large excess of sodium chloride is employed in order to prevent the decomposition of carbamide and uric acid, a study has been made of the action of dilute sodium hydroxide on solutions of uric

acid. The results show that a small, but constant, quantity of ammonia is produced, but that the presence of sodium chloride has very little effect. It is possible that other nitrogenous constituents of milk may be protected by sodium chloride, but the use of such large amounts as recommended by Steel (*loc. cit.*) does not seem to be justified.

E. G.

Estimation of Nitric Acid in Milk by means of Diphenylamine-Sulphuric Acid. J. Tillmans and A. Splittgerber (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 401—404).—In estimating nitric acid (nitrates) in milk by the process described previously (this vol., ii, 151), it is recommended that the milk be treated with its own volume of a mixture consisting of equal parts of 5% mercuric chloride solution and 2% hydrochloric acid. After filtration, 1 c.c. of the serum is mixed with 4 c.c. of the diphenylamine-sulphuric acid reagent, and the coloration produced compared with those obtained with solutions containing known quantities of nitric acid. As milk contains certain substances which prevent the full development of the coloration due to the nitric acid present, these standard solutions should be prepared by placing quantities of 0·45, 0·85, 1·2, 1·5, and 2·0 c.c. of a 0·0171% potassium nitrate solution in separate 100 c.c. flasks, adding 2 c.c. of saturated sodium chloride to each, and diluting to 100 c.c.; these solutions will then contain quantities corresponding with 1, 2, 3, 4, and 5 mg. of nitric acid (N_2O_5) respectively per litre of milk.

W. P. S.

The Accuracy of Nitrate Estimations. Siegfried Seydel and L. Wichers (*Zeitsch. angew. Chem.*, 1911, **43**, 2046—2054).—A criticism of the various methods for the estimation of nitric nitrogen now in vogue, particularly in their application to soil analysis.

Reduction in alkaline solution by means of zinc and iron gives good results if the amount of nitric nitrogen actually present does not exceed 30 mg. Densch's objection that ammonia is split off from nitrogenous organic matters present, and so affects the result, was found to be groundless. With great care, and making a check experiment side by side, Schloesing's process (measuring as nitric oxide) also gives good results in presence of organic matters (urea excepted). The results obtained by the "nitron" process are a little too low, but this method may be used even in the presence of urea and asparagine. Ulsch's process (reduction with iron in acid solution) is, according to Densch, liable to give excessive results in the presence of much organic matters; the author's confirm that statement.

Densch's indirect process cannot be recommended. L. de K.

Analysis of Nitrates. Antonio Quartaroli (*Gazzetta*, 1911, 41, ii, 53—59).—See this vol., ii, 1085.

Estimation of Phosphorus in Pig Iron and Cast Iron without Separation of Silicon. Eugen R. E. Müller (*Chem. Zeit.*, 1911, 35 1201—1202).—Four grams of the sample are placed in an Erlenmeyer flask, and boiled with 60 c.c. of nitric acid (D 1·2). When all dissolved

the liquid (which should not occupy less than 30 c.c.) is transferred to a 100 c.c. flask and made up to the mark. Twenty-five c.c. are then taken and boiled in a beaker with 2 c.c. of potassium permanganate (40 grams per litre) for two minutes, and, after cooling the beaker for ten minutes in a stream of cold water, the excess of the permanganate, together with any manganese peroxide formed, is decomposed by careful addition of sodium peroxide in small portions at the time.

The clear solution is now again heated to boiling, and then mixed with its own volume of molybdenum solution. A pure yellow precipitate is obtained, fit for direct weighing, after drying at 150°. Contrivances for cooling and filtering are described and figured in the original.

L. DE K.

Mechanicalising Analysis as an Aid to Accuracy and Speed. CHARLES H. RIDSDALE and N. D. RIDSDALE (*J. Iron Steel Inst.*, 1911, **83**, 332—374).—The rapid methods of estimating phosphorus and manganese in steel, iron, or slag have been modified by employing the oxidising and other reagents in the form of compressed solid tablets or "analoids," thus saving weighing and ensuring the uniformity of the conditions of oxidation and precipitation. C. H. D.

Estimation of Hypophosphites. ERWIN RUPP and KROLL (*Arch. Pharm.*, 1911, **249**, 493—497).—Rupp and Finck have described (Abstr., 1903, ii, 330) a process for the estimation of hypophosphites, which depends on their oxidation to phosphites and eventually to phosphates by the action of iodine. The first step in this reaction is slow, and the whole estimation occupies about twenty hours.

The authors now find that the oxidation may be accomplished much more speedily by using the standard bromine solution devised by Beckurts and Koppeschaar, which is formed by adding dilute sulphuric acid to a solution of potassium bromate and bromide of known strength. The amount of bromine solution used must be about twice that required to oxidise the hypophosphite to phosphate, and the reaction requires one hour for completion. The excess of bromine is determined by adding standard potassium iodide solution, and titrating the liberated iodine with standard thiosulphate.

T. A. H.

Method for the Detection and Estimation of Arsenic in Organic Compounds. GIUSEPPE BRESSANIN (*Boll. Chim. Farm.*, 1911, **50**, 727—730).—The arsenic in sodium cacodylate, sodium methylarsinate (arrhenal), sodium *p*-aminophenylarsinate (atoxyl), and dihydroxydiaminoarsenobenzene dihydrochloride (salvarsan) can be estimated by the author's method for arsenic in inorganic compounds, which depends on the insolubility of arsenic iodide in sulphuric acid or hydrochloric acid. In these cases, however, the substances must first be heated for about two hours with concentrated sulphuric acid in order to remove the arsenic from organic combination.

An account is also given of the behaviour of "salvarsan" towards a number of reagents. R. V. S.

Detection, Separation, and Estimation of Arsenic and Antimony. GIUSEPPE BRESSANIN (*Boll. Chim. Farm.*, 1911, 50, 691—694).—The method of estimating arsenic given by Blattner and Brasseur (Abstr., 1904, ii, 291) gives good results when applied to sulphuric acid of 45° Baumé, and also with mixtures of sulphuric and hydrochloric acids, provided that the amount of the latter is not more than one-third of that of the former; if this proportion is exceeded, loss occurs owing to partial solution of the arsenic tri-iodide by the hydrochloric acid, washing off the precipitate with the latter also causing further loss. Instead of 5 c.c. of 30% potassium iodide solution, only 2·5 c.c., or even less, should be used for the precipitation. Hence for estimating arsenic in hydrochloric acid, 1 part of this is mixed with 2 parts of pure sulphuric acid of 45° Baumé. With sulphuric acid free from tin and lead, the precipitation is effected without addition of hydrochloric acid, whilst with commercial sulphuric acid (45° Baumé) one-third of its volume of hydrochloric acid is added; if nitrous compounds are present, these must be decomposed by adding a sufficient quantity of urea crystals. For washing the precipitate, a mixture of 2 parts of sulphuric acid (45° Baumé) and 1 part of hydrochloric acid is employed. The above procedure gives results which are much nearer to the truth than Blattner and Brasseur's method, and are not vitiated if the sulphuric acid has a density as high as 50° Baumé.

The estimation of antimony in sulphuric acid can be carried out in a similar manner, but the antimony iodide is soluble in hydrochloric acid. The most suitable density of the sulphuric acid for the complete precipitation of antimony iodide is 50° Baumé, and the precipitate is freed from the iodine which separates by three washings with sulphuric acid (50°Bé.). The antimony iodide is dissolved in 10% Rochelle salt solution prior to titration.

Arsenic and antimony may be estimated simultaneously by dissolving the substance in, and making up to a known volume with, sulphuric acid of 50° Baumé. In an aliquot part of the solution, the two iodides are precipitated, and the precipitate dissolved and titrated with iodine solution as above. Another aliquot portion is mixed with one-third of its volume of hydrochloric acid, this solution yielding only arsenic tri-iodide on precipitation.

The same method is applicable to the estimation of arsenic or antimony in arsenates or antimonates. T. H. P.

Spectrophotometric Estimation of Xenon. Constancy of the Xenon-Argon and Xenon-Krypton Ratios in Natural Gaseous Mixtures. CHARLES MOUREU and ADOLPHE LEPAPE (*Compt. rend.* 1911, 153, 740—743. Compare Abstr., 1909, ii, 363; 1910, ii, 136; this vol., ii, 392, 439, 808).—The amount of xenon in mixtures of the gas with argon can be determined by a method identical in principle with that already described for krypton, the line λ 4671·42 being employed for the purpose. In this way it is possible to estimate 0·0005 cm. of the gas in 4 c.c. of a mixture. The ratio of xenon to krypton was found to be fairly constant in seventeen natural gases from thermal springs and in one from a volcano. Taking this in conjunc-

tion with the results already recorded for argon, it is shown that the constant proportions in which these gases occur resemble that of the components of a definite compound, a conclusion in harmony with the nebular hypothesis of the origin of the solar system. W. O. W.

Potassium: its Titrimetric Estimation in Small Amounts. LEON T. BOWSER (*J. Amer. Chem. Soc.*, 1911, **33**, 1752—1757).—The author has recently described a method for the detection of small quantities of potassium as the cobaltinitrite (this vol., ii, 1031). A process for the estimation of potassium has now been devised in which the metal is precipitated as dipotassium sodium cobaltinitrite, and the latter is collected and titrated with dilute potassium permanganate.

The solution in which potassium is to be estimated is evaporated nearly to dryness, and, when cold, is treated with 2·5 c.c. of sodium cobaltinitrite solution and 10 c.c. of a mixture of equal volumes of glacial acetic acid and 95% alcohol. The precipitate is collected on an asbestos filter, and washed with 20% acetic acid. The asbestos pad and precipitate are transferred to a beaker, and an excess of 0·005*N*-potassium permanganate solution is added from a burette. The mixture is boiled, acidified with sulphuric acid, and, after continuing the boiling for a moment, the excess of potassium permanganate is titrated back by means of 0·005*N*-oxalic acid. After making the necessary deduction indicated by a blank experiment, the number of c.c. of permanganate used when multiplied by 0·00004282 gives grams of K_2O, or by 0·00003554 gives grams of K.

The estimation is not affected by the presence of moderate quantities of sodium, calcium, or magnesium. The method is recommended as being simple and trustworthy for small amounts of potassium (about 50 parts per million), but cannot be used for the estimation of large quantities. E. G.

Estimation of Potassium in Urine. HARRY H. GREEN (*Bio. Chem. J.*, 1911, **6**, 69—75).—The volumetric method of estimating potassium as the cobaltinitrite, described by Drushel (Abstr., 1908, ii, 66), has been modified for the estimation of potassium in urine (compare also Drushel, Abstr., 1909, ii, 94). Twenty-five c.c. of urine are evaporated to dryness and ignited; the ash is moistened with nitric acid, and again ignited until free from organic matter and ammonium salts. It is then dissolved in water containing a little hydrochloric acid, neutralised with sodium hydroxide containing a little sodium acetate, the solution evaporated to 5—10 c.c., 1 c.c. of glacial acetic acid and 10 c.c. of the cobalt reagent, prepared as described by Adie and Wood (Trans., 1900, **77**, 1076) added, and then evaporated to crystallisation. The cobaltinitrite, $K_2NaCo(NO_2)_6,H_2O$, is freed from the brown matrix by treatment with about 50 c.c. of 10% acetic acid, washed with dilute acetic acid, dried, and then oxidised with potassium permanganate as described by Drushel (*loc. cit.*). Potassium can be estimated with equal accuracy as chloride, sulphate, nitrate, and acetate by this method, provided no free acid other than acetic is present during evaporation with the sodium cobaltinitrite reagent.

Salts of other metals have very little effect on the accuracy of the **method.**

[illegible]

The Electrolysis of Sodium Chloride with the **Mercury Cathode.** CHARLES A. PETERS (*Amer. J. Sci.*, 1911, [iv], 32, 365—385).—The author shows that in the electrolysis of sodium chloride in the Hildebrand apparatus for the electrolytic [illegible] tion of anions (Abstr., 1907, ii, 574), the anode being of silver or of silver-plated platinum, and the cathode of mercury, silver is always transferred from the anode to the cathode. Under certain conditions, which must be determined by experiment for each apparatus and strength of solution used, the amount of silver thus transferred may be neglected for analytical purposes.

It is recommended that the anode covered with silver chloride be first heated below the fusing point of the chloride to decompose the silver oxide, and that then the heat be increased so as to fuse the chloride, five or ten minutes at 400—500° being sufficient.

Sodium hydroxide is always present in the inner cell after the beginning of the electrolysis, a low current with corresponding increase in time of electrolysis producing more alkali than a high current and short time of electrolysis.

The best method for removing the fused chloride from an anode is to heat it for about twenty minutes at 500° in a current of hydrogen.

T. S. P.

Use of the Edison Accumulator in Electro-analysis. OTTO BRUNCK (*Zeitsch. angew. Chem.*, 1911, **24**, 1993—1997).—The author uses the Edison accumulator for the estimation and separation of metals which can be deposited from sulphuric acid solution with less than 1·36 volts; such metals are silver, mercury, palladium, platinum, rhodium, iridium, etc. The accumulator is connectly directly with the electrolytic apparatus, a rheostat in the circuit not being necessary (compare Foerster., Abstr., 1906, ii, 805), unless the current density exceeds 0·2 ampere per sq. dcm. A gauze cathode of 50 sq. cm. area is used.

Silver is best deposited from a sulphuric acid solution at a temperature of 80—90°, at which temperature the solubility of silver sulphate is sufficient to retain it in solution; any nitric acid present is previously expelled by evaporation with sulphuric acid. The results are quantitative in the presence of copper, arsenic, antimony, or lead. In the presence of antimony some tartaric acid must be added before the electrolysis is proceeded with, and it is not necessary to filter off any lead sulphate before depositing the silver.

The author has also used a Leclanché dry cell in place of the Edison accumulator, care being taken not to let the current density exceed 0·2 ampere per sq. dcm.; it could be used for two years without renewal, since during any electrolysis with graded potential the current gradually falls to zero.

T. S. P.

Estimation of Calcium in the Presence of Magnesium and Phosphates. Estimation of Calcium in Urine. FRANCIS H. McCRUDDEN (*J. Biol. Chem.*, 1911, **10**, 187—199).—The method

described previously by the author (Abstr., 1910, ii, 243) may be rendered more rapid as follows: the neutralised urine is acidified with hydrochloric acid, oxalic acid and sodium acetate are added, and the mixture is shaken for ten minutes or placed aside overnight. The calcium oxalate is then collected, washed, and ignited, or titrated with permanganate solution. W. P. S.

Physico-chemical Volumetric Analysis. IV. Estimation of Copper and Silver. PAUL DUTOIT and GOTTFRIED VON WEISSE (*J. Chim. phys.*, 1911, 9, 608—629).—The precipitation of copper or silver by a soluble sulphide gives a more sharply defined potential change than when other precipitants, such as sodium hydroxide, potassium ferrocyanide, or sodium thiosulphate, are employed.

Potassium sulphide containing excess of potassium hydroxide, prepared in the laboratory, was used in most of the experiments, but was found to undergo slow conversion into thiosulphate with loss of precipitating power. Crystalline sodium sulphide was afterwards found to be more stable.

The precipitation of silver by alkali sulphide proceeds normally, but copper always requires 2—3% more sulphide than theory demands. The sulphide must, therefore, be standardised against solutions of the same metal at about the same concentration as it is to be employed with. The potassium sulphide must not be weaker than $N/50$, since more dilute solutions undergo decomposition to thiosulphate at a rapid rate. Hence in the titration of small quantities of copper or silver a microburette is used.

The solutions are neutralised and acidified with acetic acid before titration. Mineral acids in the solution give rise to serious errors. The current density of the polarising current must not exceed 10^{-6} amperes. With very dilute solutions, a correction may be applied for electro-deposited metal.

Copper and silver may be titrated accurately in solutions containing 20 mg. per litre, and even traces of the order 0·1 mg. per litre can be estimated, although no visible precipitate or coloration is present.

The estimation of copper is unaffected by relatively enormous proportions of neutral salts, so that the method may be found applicable in the examination of preserved foods. R. J. C.

Quantitative Estimation of Copper in Commercial Sulphate by means of Alkali Hypophosphites. ALFREDO CAVAZZI (*Gazzetta*, 1911, 41, ii, 374—378).—The author calls attention to his publications on this subject (*Rend. R. Accad. Sci. Bologna*, 1900—1902). The solution of 2 grams of copper sulphate in about 25 c.c. of water is acidified with 12 drops of 5% sulphuric acid, 10 c.c. of 40% sodium hypophosphite are added, and the mixture is heated on the water-bath for twenty minutes. A 10% solution of sodium carbonate is then added, until no more carbon dioxide is evolved, care being taken that the hot liquid remains clear, and the heating is continued for ten minutes. While still hot, the liquid is again neutralised, the copper is collected, and weighed after ignition in a current of hydrogen. The

process is rapid and accurate, and is only interfered with (and then but slightly) by the presence of arsenic, which is infrequent.

R. V. S.

Precipitation of Zinc, Manganese, Cobalt, Nickel, Copper, and Cadmium from their Ammoniacal Solution with Sodium Carbonate and Phenyltrimethylammonium Carbonate. SCHIRM (*Chem. Zeit.*, 1911, 35, 1177, 1193—1194).—The ... the above metals to which has been added excess of ammonia ... some cases, ammonium carbonate) do not deposit the hydr... carbonates) completely on boiling, but do so when a solution of ... carbonate is added. On account of its complete volatility ... phenyltrimethylammonium carbonate may be used in preference ... the sodium salt.

The carbonates separated are completely free from sulphate ... sulphuric acid can, therefore, be entirely recovered from the ... When dealing with manganese salts, a little hydrazine hydr... should be added to prevent turbidity when adding ammonia.

L. de K.

Iron Metabolism. I. The Estimation of Small Amounts of Iron. FRIEDRICH JAHN (*Zeitsch. physiol. Chem.*, 1911, 75, 308—338).—The author has endeavoured to find a suitable method ... estimating small quantities of iron in organic substances. Neumann's so-called wet incineration method (Abstr., 1903, ii, 243; 1905, ...) should be used, any iron in the acids used being estimated and allowed for. He finds that estimation by means of potassium permanganate, hyd... acid, or stannous chloride does not lead to exact results, and prefers ... method of reducing the iron by means of a slight excess of standard titanous chloride solution, and subsequent determination of the excess by means of standard iron solution, potassium thiocyanate being used as indicator.

The effect of varying the volume of solution, and the amounts of potassium thiocyanate, iron, sulphuric and hydrochloric acids has been studied.

H. W.

Quantitative Separation of Iron and Manganese. JULES A. SANCHEZ (*Bull. Soc. chim.*, 1911, [iv], 9, 880—881).—The process depends on the fact that from a solution containing ferric and manganous salts, pyridine precipitates the iron as ferric hydroxide, leaving manganese dissolved. By this means, 0·0005 gram of manganese may be estimated in presence of 1 gram of iron.

In the case of manganese minerals, 1 gram is dissolved in ... hydrochloric acid, and the silica rendered insoluble by evaporation to dryness twice. The filtrate is nearly neutralised by sodium hydroxide, diluted to 100 c.c., pyridine added in excess, and the whole boiled during ten minutes. If manganese is present in large amount, the precipitated ferric hydroxide should be collected, washed, and re-treated.

In minerals containing metals of Group I, the latter should be removed by hydrogen sulphide, and the filtrate boiled and oxidised before adding the pyridine. Zinc is also precipitated by pyridine

although incompletely, and if this metal is present, the ferric hydroxide should be redissolved and reprecipitated by ammonia in presence of ammonium chloride. T. A. H.

Estimation of Nickel [in German Silver]. FRED IBBOTSON (*Chem. News*, 1911, **104**, 234).—0·5 Gram of the alloy is dissolved in 9 c.c. of nitric acid (D 1·2), and diluted to 400 c.c. 0·3 Gram of tartaric acid is added, and then ammonia in excess. After heating to 80°, an excess of solution of dimethylglyoxime is added.

The precipitate containing the nickel is collected on a filter, and washed with a hot solution of ammonium nitrate until the washings are colourless. As it always retains copper, it must be re-dissolved in hot dilute nitric acid (1 : 1) and re-precipitated as directed.

The precipitate whilst still wet is enclosed completely in two filters, transferred to a crucible, and heated cautiously at the mouth of the muffle or over a small flame until the outer papers are thoroughly charred. The temperature is then gradually increased to a bright red heat. L. DE K.

Precipitation of Nickel Compounds and Preparation of Spongy Nickel. WILSON H. LOW (*Analyst*, 1911, **36**, 539—540).—Nickel is not precipitated completely from its solutions either by ammonia or hydrazine on boiling, but if a solution of a nickel salt containing ammonium chloride is boiled with excess of hydrazine, the nickel is completely precipitated. When the precipitate is ignited in a current of hydrogen, spongy nickel is obtained, which, of course, is free from fixed alkali. L. DE K.

Estimation of Tungsten in Wolframite in the Presence of Molybdenite. WOLDEMAR TRAUTMANN (*Zeitsch. angew. Chem.*, 1911, **24**, 2142—2143).—One gram of the finely powdered ore is gently roasted in a platinum crucible until the odour of sulphur dioxide has gone off. The mass is then extracted three or four times with warm dilute ammonia, which dissolves the molybdenum trioxide formed. The filter, after being washed with solution of ammonium nitrate, is replaced in the crucible, and the whole is again ignited; the residue is then submitted to the ordinary fusion with sodium hydroxide, which should be done in a nickel crucible. L. DE K.

Use of Hæmatin in Qualitative Analysis and in the Volumetric Estimation of Bismuth. ETTORE VASSALLO (*Gazzetta*, 1911, **41**, ii, 204—212. Compare Moffatt and Spiro, Abstr., 1907, ii, 653).—Solutions of hæmatin, obtained by extracting logwood with alcohol, give colorations with most metals and metalloids, but only a few of these persist in faintly acid solutions. Bismuth gives an intense violet coloration, even in fairly acid solution; arsenic, antimony, and tin also give a violet coloration. Solutions of molybdenum give an intense blue coloration, which is stable towards fairly concentrated acid. Schemes of analysis are given for recognising tin and bismuth in alloys and mixtures by the

use of hæmatin test-papers. The sensibility, in presence of suitable concentrations of acid, exceeds one part in fifty thousand.

The volumetric estimation of bismuth is effected by adding a standard solution of disodium phosphate to the bismuth solution and testing the liquid for bismuth by means of the logwood test-papers at intervals. The results quoted show a positive error ranging from 0·9 to 0·1%, the variation being associated with different conditions of dilution and temperature. The best results are obtained when the solution is kept cold and also neutral. E. V. S.

Colorimetric Detection of Alcohol in Presence of Acetone. Colour Reactions of Certain Groups of Organic Compounds in Presence of Mineral Acids and Potassium Dichromate. HENRI AGULHON (*Bull. Soc. chim.*, 1911, [iv], **9**, 881—885. Compare Nicloux, Abstr., 1898, ii, 543).—The author finds that the reduction of potassium dichromate in presence of sulphuric acid by organic substances becomes more specific in character when nitric acid, phosphoric acid, or potassium hydrogen sulphate is substituted for sulphuric acid.

Potassium dichromate, 0·5 gram, dissolved in 100 c.c. of nitric acid (36°Bé) gives at once a bluish-violet coloration in the cold with substances containing a –CHO or –OH group, and with certain other compounds, such as ether, ethyl acetate, formic acid, and unsaturated fatty acids. The aliphatic ketones give a coloration, but as a rule only after some hours. Acetophenone and the quinones behave like acetone, but *cyclo*hexanone and its homologues give the coloration immediately. Certain phenols give the same colour reactions as they do with potassium dichromate alone. The reaction is less specific on warming, and under these conditions a green coloration is developed.

With phosphoric acid (60°Bé) the range of applicability is the same as with nitric acid, but the reagent is then less delicate.

With potassium hydrogen sulphate in water no coloration is produced in the cold, but a green tint is produced on warming. This is given by alcohols, aldehydes, *cyclo*hexanone, and its homologues, ether, ethyl acetate, etc., but not with aliphatic ketones, acetophenone, or unsaturated fatty acids. In this form the reagent may be used to distinguish ricinoleic acid, which contains an –OH group, from oleic and other like acids which do not. T. A. H.

Analysis of Lactic Acid. A. A. BESSON (*Chem. Zeit.*, 1911, **35**, 1209—1210).—It is shown that the total acidity of lactic acid containing lactic anhydride may be accurately estimated by neutralising the free acid, adding an excess of $N/1$-alkali, leaving the mixture at the ordinary temperature for ten minutes, neutralising the excess of alkali, adding a slight excess of $N/1$-acid, boiling, and titrating the acid. W. P. S.

Estimation of β-Hydroxybutyric Acid in Urine. ROBERT A. COOKE and E. E. GORSLIN (*J. Biol. Chem.*, 1911, **10**, 291—294).—Results of experiments carried out by the authors show that the

method described by Shaffer (Abstr., 1908, ii, 992) is trustworthy, provided that the urine is treated with an excess of basic lead acetate and ammonia before the distillation part of the process is commenced. This treatment is especially necessary in the case of urines containing large quantities of dextrose. The excess of lead should be removed before the distillation, in order to prevent "bumping."

W. P. S.

Polarimetric Method for the Estimation of Malic Acid and its Application to Cane and Maple Products (Sugars). PETER A. YODER (*Zeitsch. Nahr. Genussm.*, 1911, **22**, 329—350).—The method depends on the increase in the rotatory power of malic acid when the acid is treated with uranium salts. A solution of malic acid containing 1 gram per 100 c.c., when converted into the uranium compound by the addition of uranium acetate in the proportion of at least 1·25 atoms of uranium to 1 molecule of malic acid, has a rotatory power of $-29·7°$ Ventzke at 20°C. for white light, or $-28·9°$ for sodium light. The presence of organic acids, with the exception of optically active hydroxydicarboxylic acids, does not, within certain limits, have any great influence, and sugars, such as sucrose, dextrose, and lævulose, have no effect; mineral acids, however, seriously affect the rotatory power of the malic acid–uranium compound. The rotatory power decreases by 0·03° Ventzke for each 1° rise in temperature. In the case of a 1% solution of tartaric acid, the uranium compound has a rotatory value of $+26·1°$ Ventzke. For the estimation of malic acid in sugar-cane and maple products, 50 grams of the syrup, or a mixture of 33·33 grams of sugar with 16·66 c.c. of water, are neutralised, diluted with water to a weight of 65 grams, and treated with 10 c.c. of lead acetate solution, D 1·25. After the addition of 150 c.c. of 95% alcohol, the mixture is set aside for three hours, then filtered, and the precipitate washed with 75% alcohol. The precipitate is treated with hydrogen sulphide, the lead sulphide is removed by filtration, the filtrate is evaporated to a volume of about 30 c.c., and then diluted to 50 c.c. The rotatory power of 20 c.c. of this solution is determined before and after the addition of uranium acetate, the mixture being neutralised in the latter case, and allowance made for the alteration in volume. The percentage quantity of malic acid, x, present, is calculated from the formulæ: for white light,

$$x = \frac{(P_1 - P) \times [1 + 0·001(t - 20)]}{-29·6 \times 0·5L},$$

or, for sodium light, $x = \frac{(P_1 - P) \times [1 + 0·001(t - 20)]}{-28·8 \times 0·5L}$, where P and P_1 are the rotatory powers before and after treatment with uranium acetate respectively, and L the length of the polarimeter tube in dcm. Barium acetate may be employed in place of lead acetate in the process. Sugar-cane syrup was found to contain 0·02% of malic acid, and maple syrup from 0·26 to 0·51%. If the total acidity, n, expressed in c.c. of $N/1$-alkali be known, malic and tartaric acids may be estimated in mixtures of the same; let the increase in the rotatory power at 27·5° in a 20 cm. tube be $m°$ Ventzke, x the percentage of malic acid, and y

the percentage of tartaric acid, then $n = \frac{x}{0{\cdot}06703} + \frac{y}{0{\cdot}07[illegible]}$ [illegible] $m = 25{\cdot}16y - 29{\cdot}27x$, or, $x = 0{\cdot}03287n - 0{\cdot}01741m$ and $y =$ [illegible] $0{\cdot}01949m$.

W. P. S.

Detection of Benzoic Acid in Foods. EDUARD [illegible] (*Arbeit. Kaiserl. Gesundheitsamte*, 1911, **38**, 149—154; [illegible]
I. *Estimation of the Total Benzoic Acid in Cranberries, etc.*—The cran-berries are heated with alcohol for one hour, the mixture is then treated with an excess of sodium hydroxide, filtered, the filtrate evaporated to remove alcohol, and the residue is extracted with a mixture of ether and light petroleum, after being acidified with sulphuric acid. The ethereal extract is then shaken with dilute sodium hydroxide solution, and the alkaline aqueous extract contain-ing the benzoic acid is treated with potassium permanganate as described by Heide and Jakob (Abstr., 1910, ii, 359). The benzoic acid is next extracted with ether, the ethereal solution is evaporated, the residue is re-dissolved in a small volume of ether, transferred to a test-tube, and after the ether has been evaporated, the benzoic acid is sublimed on to the upper sides of the tube. The lower portion of the tube is then cut off, and the benzoic acid is dissolved in alcohol and titrated. The amount of benzoic acid found in various samples of cranberries varied from 0·089 to 0·206% (compare Abstr., [illegible] ii, 440).

II. *Detection of Benzoic Acid in Wine.*—The method of separating benzoic acid from wine described by Heide and Jakob (*loc. cit.*) was found to be trustworthy; it is recommended, however, that the wine be filtered, after being evaporated in the presence of alkali and then acidified, previous to the extraction with ether. The benzoic acid obtained may be identified by fusing it for not longer than three minutes with potassium hydroxide, and testing the resulting salicylic acid with ferric chloride.

W. P. S.

Detection of Benzoic Acid in Margarine, Butter, and Other Fats. WALTHER FRIESE (*Pharm. Zentr.-h.*, 1911, **52**, 1201—12[illegible]).—One hundred grams of the fat are mixed thoroughly with 25 c.c. of a 20% sodium carbonate solution, and the mixture is melted on a water bath. After cooling, the aqueous layer is separated, treated with an excess of 10% barium chloride solution, the barium precipitate is collected on a filter, and the excess of barium is removed from the filtrate by the addition of sulphuric acid. The benzoic acid is then extracted from the acid solution with ether, and the residue obtained on evaporating the ethereal solution is tested for benzoic acid, prefer-ably by heating the residue with alcohol and sulphuric acid; any benzoic acid present is thus converted into ethyl benzoate, which may be identified by its odour.

W. P. S.

Kobert's Reagent as a Test for Salicylic Acid. JOHN McCRAE (*Analyst*, 1911, **36**, 540—541).—Kobert's morphine reagent (sulphuric acid containing one drop of formaldehyde solution per c.c.) gives a charac-teristic rose colour with salicylic acid or salicylates. The reaction is

most clearly seen when about 1/50 mg. is dissolved in two drops of sulphuric acid and a drop of the reagent then added. The test also works with *o*-acetoxybenzoic acid (aspirin) and salol.

Salicin gives a red colour with sulphuric acid alone, but if to the solution is added a drop of the reagent in such a way that mixing does not occur, a much deeper and richer red is developed.

Kobert's reagent also gives characteristic colorations with the following substances: Phenol, reddish-violet; catechol, violet (redder than the colour obtained with morphine); resorcinol, deep orange-brown: quinol, dirty greenish-brown; pyrogallol, brown; α-naphthol, dirty green; β-naphthol, dirty brown; cinnamic acid, brown; mandelic acid, yellow. L. DE K.

The Purification and Analytical Control of Potassium Ferrocyanide. KARL SCHRÖDER (*Zeitsch. anorg. Chem.*, 1911, **72**, 89—99. Compare Müller and Diefenthäler, Abstr., 1910, ii, 910).—Potassium ferrocyanide has the composition $K_4Fe(CN)_6,3H_2O$ even when crystallised from boiling solution, but in drying it is necessary to expose as small a surface as possible, or oxidation and loss of water take place.

Iron is best estimated in potassium ferricyanide by heating with concentrated sulphuric acid, finally raising the temperature to the boiling-point of the acid, dissolving in water and hydrochloric acid, and precipitating with cupferron (ammonium nitrosophenylhydroxylamine), igniting in a quartz crucible. The precipitate is free from alkali.

For the standardisation of permanganate solutions, the solution of potassium ferrocyanide (2 grams) is added to 100 c.c. of a cold saturated solution of mercuric chloride, and the precipitate obtained is then dissolved in 200 c.c. of the same solution, acidified with hydrochloric acid, and heated to boiling. After cooling, 30 c.c. of a solution prepared from 100 grams of manganous sulphate, 200 c.c. of concentrated sulphuric acid, and 200 c.c. of phosphoric acid, D 1·7, to the litre, are added. The values obtained on titrating with permanganate are slightly high, averaging 100·12%. C. H. D.

Apparatus for the Estimation of Amino-groups. DAVID KLEIN (*J. Biol. Chem.*, 1911, **10**, 287—289). An apparatus is described for use in the estimation of aliphatic amino-groups by the process proposed by van Slyke (this vol., ii, 944). W. P. S.

Estimation of Nicotine in Tobacco Extracts. W. KOENIG (*Chem. Zeit.*, 1911, **35**, 1047—1048).—A reply to Tóth (this vol., ii, 943), who complains that the solutions of nicotine in toluene obtained in the author's extraction process cannot be examined polarimetrically on account of their dark colour. The author states he has never experienced any trouble in that respect with the various polariscopes.

Xylene is also a very good solvent for nicotine. The specific rotation of nicotine in a dilute xylene solution is +173°. Other

objections to the process are also overruled, but it must be understood that the method applies to extracts only and not to tobacco.

L. DE K.

Estimation of Codeine in Opium. ALBERT E. ANDREWS (*Analyst*, 1911, **36**, 489—490).—In the process described, the opium is extracted thoroughly with cold water, and the solution is treated with lead acetate to remove colouring matters, etc., and narcotine. Sodium salicylate is then added in order to precipitate thebaine and any remaining resinous substances, and the filtered liquid is concentrated and shaken with ether to remove substances which are soluble in this solvent. The morphine is then "fixed" by the addition of a large excess of sodium hydroxide, and the codeine is extracted with ether. The ethereal solution of the alkaloid is evaporated at a low temperature, the residue is dried under reduced pressure, and weighed. The dry alkaloid may also be titrated with $N/10$-acid, using litmus as the indicator. W. P. S.

A Reaction of Sparteine. ARMAND JORRISEN (*J. Pharm. Chim.*, 1911, [vii], **4**, 251—252).—A reaction which distinguishes sparteine from other alkaloids consists in adding a small quantity of sulphur to an ethereal solution of the alkaloid, and treating the mixture with hydrogen sulphide. A bright red, bulky, precipitate in formed, which disappears on the addition of water. The precipitate is readily distinguished from those given by coniine and atropine under similar conditions; the former yields an orange-coloured precipitate and the latter a yellow precipitate. W. P. S.

A Modification of Nakajama's Reaction for Bile Pigment in Urine. A. A. VON MASLOFF (*Zeitsch. physiol. Chem.*, 1911, **74**, 297—298).—The reaction is intensified by the addition of a few drops of hydrogen peroxide. W. D. H.

Estimations of Globulin by means of Ammonium Sulphate and the Preparation of Pure Globulins. HUGO WIENER (*Zeitsch. physiol. Chem.*, 1911, **74**, 29—66).—The usual methods of fractionating serum proteins by ammonium sulphate are regarded as valueless, and give the amount of globulin too high. If the total protein is increased, the rise appears to fall on the globulin for this reason; hence clinical investigations of this nature need entire revision. The error is greatly minimised by diluting the serum first. W. D. H.

Effect of Heat on the Peroxydase in Cow's Milk. J. J. VAN ECK (*Chem. Weekblad*, 1911, **8**, 691—702; *Zeitsch. Nahr. Genussm.*, 1911, **22**, 393—400).—The author describes an apparatus adapted to determining the diminution in the proportion of active peroxydase in milk caused by heating at different temperatures.

A. J. W.

INDEX OF AUTHORS' NAMES.

TRANSACTIONS, PROCEEDINGS, AND ABSTRACTS
1911.

(Marked T., P., and A., i and A., ii respectively.)

A.

F.

G.

H.

J.

Q.

T.

U.

W.

Y.

Z.

INDEX OF SUBJECTS.

TRANSACTIONS, PROCEEDINGS, AND ABSTRACTS.

1911.

(Marked T., P., and A., i and A., ii respectively.)

A.

D.

E.

H

J.

K.

M.

P.

R.

T.

V.

(*o-Xylene*, *Me* : *Me* = 1:2 ; *m-xylene*, *Me* : *Me* = 1 3 ; *p-xylene*, *Me*

ERRATA.

COLLECTIVE INDEX 1893 1902.

PART II. SUBJECTS.

Col.
ii *delete* "isoindol 53."
ii ,, "GABRIEL and NEUMANN, 1893, A., i, 346."
i ,, "See 2 : 5-Diphenylpyrazine."
i *insert* "(GABRIEL and NEUMANN, 1893, A., i, 346

VOL. LXXXVI (ABSTR., 1904).

PART I.

r "Malonobenzylamic," *read* "Malobenzylamic."

,, "SANDERS" *read* "GANDERS."

NH·CH

,, "$CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot C$" *read*

CH·N

NH·CH"

"$CO_2H \cdot CH(NH_2) \cdot CH_2 \cdot C$" .

CH·N

VOL. XC (ABSTR., 1906).

PART I.

a "*Chlorohistidinecarboxylic*" read "*Chlorohistinecarboxylic.*"

,, "*histidinecarboxylic*" read "*histinecarboxylic.*"

VOL. XCIV (ABSTR., 1908).

PART I.

r "chlorohistidinecarboxylic" *read* "chlorohistinecarboxylic."

,, "nitrate" *read* "nitrite."
,, "cinnamylideneacetophenonehydroxylamine" *read* "hydroxylaminocinnamylideneacetophenoneoxime."

PART II (INDEX).

Col.
ii *for* "A., ii, 590" *read* "A., i, 595."

VOL. XCVI (ABSTR., 1909).

PART II.

Page	Line	
246	5*	*for* "mammellated" *read* "mamillated."
218	17*	,, "von Rath" *read* "vom Rath."
589	8*	,, "syenite" *read* "sodalite."
745	13*	*insert* "Rhodesia" *before* "Broken Hill."
745	8*	*for* "orthorhombic" *read* "anorthic."
745	7*	*insert* "optic" *before* "axial angle."
1026	16*	*for* "Corinth" *read* "Carinthia."

PART II (INDEX).

Page	Line	Col.	
1149	31	ii	for "*William*" read "*Walter*."

VOL. XCVIII (ABSTR., 1910).

PART I.

Page	Line	
292	8	*for* "**Formation**" *read* "**Function**."
350	9*	,, "JOSE R. CARRACIDO" *read* "JOSE RODIGUEZ CAR
562	17*	,, "$C_{10}H_{10}O_2N_3$" *read* "$C_{10}H_{13}O_2N_3$."

PART II.

46	17	*for* "Br_2O_3" *read* "Bi_2O_3."
137	11, 14	,, "granite" *read* "garnet."
137	16	,, "Gibbsite" *read* "hibschite."
312	4*	,, "210" *read* "221."
668	16	,, "Grignard" *read* "Guignard."
967	23	,, "amorphous" *read* "isomorphous."
968	4	,, "kammereite" *read* "kämmererite."
968	10	,, "$R''_3(R'_2)^{vi}Si_3O_4$" *read* "$R''_3R'''_2Si_3O_{12}$."
969	20	,, "Rhen-" *read* "Rhenish."

PART II (INDEX).

1362	4—9	Col. i	*these two entries should be under* "**Glutaconic aci**

VOL. C (ABSTR., 1911).

PART I.

36	20*	*for* "462" *read* "174."
116	21*	,, "glycol" *read* "glycine."
157	23	,, "1-phenylquinoline" *read* "2-phenylquinoline."
181	20*	,, "REYNAUD" *read* "RAYNAUD."
211	9*	,, "GIUSEPPE" *read* "GUIDO."
211	22	,, "4-*chloro*-1-*methyl*cyclo*hexan*-2-*one*" read "4-*chloro*-1-*methyl*cyclo
225	16*	,, "REITENSTEIN" *read* "REITZENSTEIN."
230	5	,, "$C_{15}H_{12}ON_2$" *read* "$C_{13}H_{12}ON_2$."
238	5*	,, "*Aminomethylglyoxaline*" read "*Aminometh*
257	15	,, "increasing" *read* "decreasing."
359	2	,, "$C_2H_8ON_2$" *read* "$C_2H_3ON_{10}$."

for "**4-m-*Xylenazo-5-hydroxy-4-*[illegible]**" *read* "**4-m-Xyl**[illegible]."
,, "***furfuran-2-carboxylic***" *read* "[illegible]"
,, "GRISCHKEWITSCH-FROCHIMOWSKY" *read* "GRISHKEWITSCH-TROCHIMOWSKY."

,, "O<CO·C:N·C·CR / N=CPh·CMe:N>NR" *read* "O<CO·C:N·C·CR / N=CPh·NMe·N>CR."

,, "NMe·CMe / NPh·CO>C:N·C<CO·NH / CO·NH>CO" *read* "NMe·CMe / NPh·CO>C:N·C<CO·NH / CO·NH>CO."

,, "LOWEY" *read* "LOWY."

PART II.

for "TAKAHASHI" *read* "TAKAHASHI."
,, "**Alkali-earths**" *read* "**Alkali-earth Metals**."
,, "GOEBEL" *read* "GAEBEL."
,, "**Ion**" *read* "**Iron.**"
,, "**Nitrosulphonic**" *read* "**Nitrososulphonic.**"
[illegible] 12 *for* "$Ba_3As_2O_8,6H_2O$" *read* "$Ba_3As_2S_6,6H_2O$."
,, "$Ba_3As_2O_8$" *read* "$Ba_3As_2S_6,6H_2O$."
The equation should [illegible]

"$3Ba(SH)_2 + As_2S_3 = Ba_3As_2S_6 + 3H_2S$."

,, "BROWING" *read* "BROWNING."
,, "**Execreted**" *read* "**Excreted**."
,, "HEIDUSKA" *read* "HEIDUSCHKA."
[illegible] *read* [illegible]
,, "JAVILLIER" *read* "JAVILLIER."
[illegible] ,, "remain in the disintegration of which" *read* "remain, in the disintegration of which."
,, "than" *read* "that."
"**21**" *read* "**22**."

PART II (INDEX).

[illegible] i., under "**German Silver**" *add* "estimation of nickel in (IBBOTSON), A., i, 1139."

* From bottom.